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PREFACE

THIS REPORT SUPERSEDES AMMRC MS 75-1 (AS-A007 270)

PURPOSE - The increasing demand for engineering materials in high temperature applications has led to investigation of the use of ceramic materials in such applications. Silicon nitride has emerged as a ceramic material having outstanding corrosion resistance, thermal shock resistance, mechanical properties and chemical properties. Although the requirements for increasingly higher operating temperatures (2500 F) for gas turbines have created much of the interest in silicon nitride, there are other potential high temperature applications such as bearings and radomes for which silicon nitride is also under consideration.

The purpose of this bibliography is to summarize the research and development accomplished to date on the fabrication and properties of silicon nitride, particularly as it applies to structural uses of the material.

This bibliography is an attempt to present a comprehensive but not an exhaustive study of the literature in the field.

TIME PERIOD - The time period emphasized in the bibliography is 1961-1976, however, material prior to this period, as well as a few historic references, are included.

SCOPE - The scope of this bibliography includes work reported in the literature on the fabrication and properties of reaction-sintered and hot-pressed silicon nitride. Also included is work on silicon oxynitride and Si-M type oxynitrides having the silicon nitride structure. Whisker growth, chemical reactions, mechanical behavior, and other related topics relevant to the processing and applications of silicon nitride are also included.

Standard bibliographic reference tools including

British Technology Index
British Ceramic Abstracts
Ceramic Abstracts
Chemical Abstracts
Defense Documentation Center, Technical Abstract Bulletin (TAB)
International Aerospace Abstracts
Metals Abstracts
NASA Scientific and Technical Aerospace Reports (STAR)
U.S. Atomic Energy Commission, Nuclear Science Abstracts
U.S. Government Reports Announcements (GRA)

were the basic sources of information. Further references were found in texts, especially those publications covering the proceedings of conferences in the field.

LIMITATIONS - The vast body of literature on the preparation and properties of thin films of silicon nitride for electronic applications has been omitted because of its formidable size and because of its marginal relevance to the applications being considered.

ACKNOWLEDGMENTS - The technical assistance of Dr. William Croft, and the persevering efforts of Miss Michelle Matte in providing many of the references and her diligent proofreading of the manuscript, are gratefully acknowledged. The editorial and typing assistance of Mrs. Jeanne Pigeon are also gratefully acknowledged.

BOOKS

1. **Arrol, W. J., "The Sialons - Properties and Fabrication", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1975), pp 729-738.**

   Physical and chemical properties of Si-Al-O-N ("Sialon") materials are presented. Comments are made on the hot-pressing and sintering characteristics of these materials.

2. **Ashcroft, W., "The Tensile and Bend Strengths of Silicon Nitride and Hot-Pressed Silicon Carbide", Special Ceramics, Volume 6, proceedings of the 6th Symposium on Special Ceramics held by the BCRA, Stoke-on-Trent, England, 9-11 July 1974, edited by P. Popper, British Ceramic Research Association, Manchester, England (1975), pp 245-260.**

   Bend strengths in air of hot-pressed and reaction-sintered Si_3N_4 were measured to 1450 C and results are related to structure and composition. Tensile test apparatus is described and results are given for short-term measurements on hot-pressed Si_3N_4. Tensile and bend data are compared in terms of Weibull concepts.

3. **Atkinson, A., and Moulson, A. J., "Some Important Variables Affecting the Course of the Reaction Between Silicon Powder and Nitrogen", Science of Ceramics, Volume 8, British Ceramic Society, Stoke-on-Trent, England (1976), pp 111-121.**

   System for gravimetric measurement of nitridation kinetics is described. Fe at 50 ppm level affects nitridation of high purity Si powder. Effects of Fe content and N pressure on microstructure are considered in detail.

4. **Baratta, F. I., Driscoll, G. W., and Katz, R. N., "The Use of Fracture Mechanics and Fractography to Define Surface Requirements for Si_3N_4", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1975), pp 445-476.**

   Internal or subsurface fracture initiation in hot-pressed Si_3N_4 was studied to establish critical defect sizes, fracture toughness, and failure strength. Data were used to establish surface finish criteria for various test systems.

5. **Barnby, J. T., and Taylor, R. A., "The Fracture Resistance of Reaction-Sintered Silicon Nitride", Special Ceramics, Volume 5, proceedings of the 5th International Symposium on Special Ceramics held by the BCRA, Stoke-on-Trent, England, 14-16 July 1970, edited by P. Popper, British Ceramics Research Association, Manchester, England (1972), pp 311-328.**

   The fracture toughness of reaction-bonded Si_3N_4 was measured in terms of K_{Ic}, the critical stress intensity factor for the onset of cracking from a defect. Toughness was measured as a function of density and the α- and β-phase contents of the Si_3N_4. Density, Young's modulus, and plain bar bend strengths were also determined.

6. **Baumgartner, H. R., "Evaluation of Roller Bearings Containing Hot-Pressed Silicon Nitride Rolling Elements", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1975), pp 713-728.**

   Rolling contact fatigue tests on hot-pressed Si_3N_4 containing bearings showed no failure at 600 k psi for up to 93 M stress cycles. Two types of bearings - one with steel races and Si_3N_4 rollers and the other with Si_3N_4 races and rollers - were successfully tested under accelerated conditions, i.e., 10,000 rpm and 2,500 lb load.

7. **Baumgartner, H. R., "Hot Pressed Silicon Nitride in Roller Bearing Applications", Materials on the Move, proceedings of the Sixth National SAMPE Technical Conference, Society for the Advancement of Material and Process Engineering, Azusa, California (1974), pp 439-443.**

Hot-pressed Si_3N_4 was evaluated by means of fatigue testing on elemental components and testing of full-scale prototypes of bearings. Si_3N_4 has excellent fatigue life. Two types of precision 55-mm-bore roller bearings were designed, fabricated, and successfully tested under accelerated test conditions.

8. **Baumgartner, H. R., and Richerson, D. W., "Inclusion Effects on the Strength of Hot-Pressed Si_3N_4", Fracture Mechanics of Ceramics, Volume 1: Concepts, Flaws, and Fractography, edited by R. C. Bradt, D.P.H. Hasselman, and F. F. Lange, Plenum Press, New York and London (1974), pp 367-386.**

Fractographic studies of hot-pressed Si_3N_4 showed that room temperature strength is controlled by various types and sizes of inclusions. In test samples without severe surface damage most fracture originated internally at inclusions. The strength of Si_3N_4 was significantly increased with reduction of the size and frequency of inclusions.

9. **Baumgartner, H. R., and Wheildon, W. M., "Rolling Contact Fatigue of Hot-Pressed Silicon Nitride Versus Surface Preparation Techniques", Surface and Interfaces of Glass and Ceramics, Volume 7, Materials Science Research, edited by V. D. Frechette, W. C. LaCourse, and V. L. Burdick, Plenum Press, New York and London (1974), pp 179-193.**

Hot-pressed Si_3N_4 fails by spalling in a manner similar to bearing steels. Pores, inclusions, and residual grinding damage nucleate fatigue cracks. Their reduction should result in increased performance. The surface condition of Si_3N_4 is critical to rolling contact fatigue life.

10. **Blegen, K., "Equilibria and Kinetics in the System Si-N and Si-N-O", Special Ceramics, Volume 6, proceedings of the 6th Symposium on Special Ceramics held by the BCRA, Stoke-on-Trent, England, 9-11 July 1974, edited by P. Popper, British Ceramic Research Association, Manchester, England (1975), pp 223-244.**

The Gibbs free energies of formation of β-Si_3N_4 and Si_2ON_2 were determined at various temperatures. The Si-O-N system is discussed in terms of an equilibrium diagram with N and O pressures as variables. Conditions for the formation of α- and β-Si_3N_4 were examined experimentally and it was found that the α-phase is formed by a vapor phase mechanism and the β-phase by a direct reaction of N and Si. The latter is the thermodynamically stable phase at all temperatures.

11. **Booher, C. R., Jr., and Roughgarden, J. D., "Design and Analysis of a Stationary Gas Turbine Ceramic Vane Assembly", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1975), pp 79-122.**

First row stator elements for 30 MW gas turbine were designed and machined from Si_3N_4 and SiC. Discussion includes ground rules, philosophy, criteria, concepts, heat transfer, contact stresses, and thermal analyses as related to design.

12. **Bratton, R. J., and Holden, A. N., "Ceramics in Gas Turbines for Electric Power Generation", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1975), pp 37-60.**

Overview of progress on program aimed at application of ceramics to industrial gas turbines for electrical power generation.

13. **Brennan, J. J., "Increasing the Impact Strength of Si_3N_4 Through Fibre Reinforcement", Special Ceramics, Volume 6, proceedings of the 6th Symposium on Special Ceramics held by the BCRA, Stoke-on-Trent, England, 9-11 July 1974, edited by P. Popper, British Ceramic Research Association, Manchester, England (1975), pp 123-134.**

The use of Ta wire reinforcements increased the Charpy impact strength of hot-pressed Si_3N_4 from 0.68-21.7 J (0.5-16 ft-lb) between room temperature and 1300 C. The mode of fracture was affected in such a way that interfacial splitting occurred together with ductile wire elongation. The Ta-Si_3N_4 composite system also exhibited a threshold energy, below which no damage occurs upon impact, that is considerably higher than that of the unreinforced Si_3N_4.

14. **Brown, R. L., Godfrey, D. J., Lindley, M. W., and May, E.R.W., "Advances in the Technology of Silicon Nitride Ceramics", Special Ceramics, Volume 5, proceedings of the 5th International Symposium on Special Ceramics held by the BCRA, Stoke-on-Trent, England, 14-16 July 1970, edited by P. Popper, British Ceramic Research Association, Manchester, England (1972), pp 345-360.**

Discussion of progress in reaction-bonded Si_3N_4 in three areas: (1) the achievement of high strength (300 MN/m^2) in Si_3N_4 prepared from flame-sprayed Si, (2) the potential of fiber reinforcement as a means of achieving high strength, high breaking strain, and fracture toughness in Si_3N_4, (3) the production of a mouldable form of Si powder compact by the use of polymeric additives.

15. **Burke, J. J., Gorum, A. E., and Katz, R. N., eds., Ceramics for High Performance Applications, proceedings of the 2nd Army Materials Technology Conference, Hyannis, Massachusetts, 13-16 November 1973, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1975).**

Collection of 36 papers presented at the conference. Pertinent papers are annotated in this bibliography with each entry under the name of the specific author.

16. **Canteloup, J., and Mocellin, A., "Synthesis of Ultrafine Nitrides and Oxynitrides in R. F. Plasma", Special Ceramics, Volume 6, proceedings of the 6th Symposium on Special Ceramics held by the BCRA, Stoke-on-Trent, England, 9-11 July 1974, edited by P. Popper, British Ceramic Research Association, Manchester, England (1975), pp 209-222.**

Si and Al powders were nitrided with NH_3 to produce ultrafine AlN, Si_3N_4, and Si-Al-O-N powders. Equipment design and powder characteristics are discussed.

17. **Chin, J., and Elsner, N. B., "Preparation of Silicon-Aluminum-Nitrogen Compounds by Reactive Ion Plating", Proceedings of the Conference on Chemical Vapor Deposition, Fifth International Conference, 1975, edited by J. M. Blocher, Jr., H. E. Hintermann, and L. H. Hall, The Electrochemical Society, Princeton, New Jersey (1975), pp 241-257.**

(Si, Al) N alloys were deposited by reactive ion plating from Si and Al evaporation and NH_3 or NH_3 + 1% SiH_4 gas mixtures. The deposits had large columnar grains composed of smaller 0.2-0.6 μm grains. At substrate temperatures of 100-300 C during deposition there were no observable differences in the morphology of the deposits. Adhesion of the deposits was good. Deposition rates were comparable to those for high-temperature CVD processes.

18. **Chiu, Y. P., and Dalal, H., "Lubricant Interaction with Silicon Nitride in Rolling Contact Applications", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1975), pp 589-608.**

Fabrication response of Si_3N_4 is similar to that of M50 tool steel presently used for aircraft engine bearings. Si_3N_4 can be satisfactorily lubricated by hydrocarbon and ester-base lubricants at temperatures to 260 C.

19. **Coe, R. F., Lumby, R. J., and Pawson, M. F., "Some Properties and Applications of Hot-Pressed Silicon Nitride", Special Ceramics, Volume 5, proceedings of the 5th International Symposium on Special Ceramics held by the BCRA, Stoke-on-Trent, England, 14-16 July 1970, edited by P. Popper, British Ceramic Research Association, Manchester, England (1972), pp 361-376.**

The properties and applications of hot-pressed Si_3N_4 of a higher strength form are discussed. The powder used in the hot-pressing operation is essentially 100% α- and the transformation to β- takes place during the densification.

20. **Davidge, R. W., Evans, A. G., Gilling, D., and Wilyman, P. R., "Oxidation of Reaction-Sintered Silicon Nitride and Effects on Strength", Special Ceramics, Volume 5, proceedings of the 5th International Symposium on Special Ceramics held by the BCRA, Stoke-on-Trent, England, 14-16 July 1970, edited by P. Popper, British Ceramic Research Association, Manchester, England (1972), pp 329-344.**

Specimens of reaction-sintered Si_3N_4 (α/β ratio ~50/50), density 2.53×10^3 kg m^{-3}, were oxidized in air at temperatures from 1000 to 1400 C and characterized by measurements of weight gain, X-ray diffraction, and microscopy. The major oxidation product is cristobalite which forms around internal pores (Stage I) and eventually as a dense surface layer (Stage II). Strength was measured as a function of temperature after direct cooling from the oxidation temperature and after temperature cycling. Oxidation in Stage I has a small beneficial effect on strength at all temperatures, whereas oxidation in Stage II has a larger beneficial effect provided that the specimen is not cooled through the cristobalite inversion temperature at ~250 C.

21. **Engel, W., Gugel, E., and Thuemmler, F., "Fluage du niture de silicium aux Temperatures elevées", Science of Ceramics, Volume 7, Societé Francaise de Ceramique, Paris (1973), pp 415-416.(Abstract)**

Four-point bending apparatus was used to study creep of hot-pressed and reaction-sintered Si_3N_4 at 1200-1400 C. The primary creep stage is very marked. Creep curves are described by a power function of time. High temperature deformation of hot-pressed Si_3N_4 occurs by grain boundary sliding.

22. **Evans, A. G., "High-Temperature Slow Crack Growth in Ceramic Materials", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1975), pp 373-396.**

High-temperature slow crack growth processes in several ceramic systems, including Si_3N_4 at >1000 C, were examined under static and cyclic loading conditions. Data obtained at temperatures up to 1400 C are used for failure prediction and analysis of slow crack growth phenomena. Purity significantly affects slow crack growth and low frequency cycling does not affect its rate. Semiquantitative mechanisms that are discussed include dislocation motion and grain boundary sliding.

23. **Evans, A. G., and Sharp, J. V., "Transmission Electron Microscopy of Silicon Nitride", Electron Microscopy and Structure of Materials, proceedings of the 5th International Materials Symposium held at University of California, Berkeley, 13-17 September 1971 , edited by Gareth Thomas, University of California Press, Berkeley (1972), pp 1141-1154.**

Thin films of reaction-sintered Si_3N_4 in both the as-fabricated condition and after deformation at 1400 C were examined in the Harwell MV microscope. The as-fabricated material consisted primarily of large grains of β-Si_3N_4 in a fine-grained matrix of α-Si_3N_4 and pores which usually contain fibers. The fibers have the α-Si_3N_4 structure often with an amorphous layer. The deformed material contained some heavily dislocated grains of β-Si_3N_4. Most dislocations have a Burgers vector <0001> and the remainder a vector of ~ <1123>. The observation of dislocation activity in the vicinity of cracks indicated that dislocation motion near the cracks contributes to the fracture surface energy.

24. **Ezis, A., "The Fabrication and Properties of a Slip-Cast Silicon Nitride", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1975), pp 207-222.**

Preparation of slip comprising Si powder suspended in H_2O with the aid of an alkaline deflocculent is described. Important variables include particle size, aging of slip, pH, and specific gravity. Correlations are discussed between processing variables and properties of resultant reaction-sintered Si_3N_4.

25. **Fate, W. A., "Pulsed Ultrasonic Measurements in Ceramic Materials at High Temperatures", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1975), pp 687-696.**

Experimental methods for MHz frequency, pulsed ultrasonic measurements at high temperatures are reviewed. Elastic property data are presented for Si_3N_4, SiC, and a Li-Al-Si glass ceramic.

26. **Gebhardt, J. J., Tanzilli, R. A., and Harris, T. A., "Chemical Vapor Deposition of Silicon Nitride", Proceedings of the Conference on Chemical Vapor Deposition, Fifth International Conference, 1975, edited by J. M. Blocher, Jr., H. E. Hintermann, and L. H. Hall, The Electrochemical Society, Princeton, New Jersey (1975), pp 786-800.**

Reaction of $SiCl_4$ and SiF_4 with NH_3 at 1-10 torr gave deposits which were glassy at 1100 C and which were crystalline α-Si_3N_4 at 1500 C. Deposits showed preferred orientation and residual stresses. Material had outstanding resistance to oxidation and creep.

27. **George, W., and Vaughan, G. N., "Calculation of Thermal Stresses in Tubular Ceramic Components", Science of Ceramics, Volume 7, Societé Francaise de Ceramique, Paris (1973), pp 87-104.**

Stresses in reaction-sintered Si_3N_4 and other materials were calculated to determine the heat fluxes necessary to give maximum tensile stresses approximately equal to the tensile strength of the material. A one-dimensional finite element stress analysis was used to estimate stresses within 12%.

28. **Godfrey, D. J., and May, E.R.W., "The Resistance of Silicon Nitride Ceramics to Thermal Shock and Other Hostile Environments", Ceramics in Severe Environments, Volume 5 of Materials Science Research, proceedings of the 6th University Conference on Ceramic Science, North Carolina State University at Raleigh, December 7-9, 1970, edited by W. Wurth Kriegel and Hayne Palmour III, Plenum Press, New York (1971), pp 149-162.**

The properties of Si_3N_4 ceramics relevant to thermal shock are described, and results of testing and hardware trials are discussed. The technology of Si_3N_4 materials, and their potential for other hostile environments, is reviewed.

29. **Godfrey, D. J., and Parr, N. L., "A Consideration of the Possible Use of Refractory Ceramic Materials for Advanced Combustion Chamber Design", Proceedings of the International Symposium on Combustion, edited by I. E. Smith, Pergamon Press, New York (1968), pp 379-397.**

Ceramic materials that are strong and stable against oxidation at high temperatures have not been used extensively, because of their brittleness. The properties of candidate ceramic materials are presented and reviewed critically, as are the fabrication processes, in regard to future requirements for combustion chambers. Possible use of Si_3N_4 ceramics up to 1600 C is discussed and the potentialities of currently available fabrication techniques are described and illustrated.

30. **Godfrey, D. J., and Pitman, K. C., "Some Mechanical Properties of Silicon Nitride Ceramics: Strength, Hardness and Environmental Effects", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1975), pp 425-444.**

Strength of reaction bonded Si_3N_4 is independent of maximum nitriding temperature (1350 C vs 1450 C) but it is dependent upon porosity. Oxidation at 1250 C reduces strength. Additions of Al_2O_3 reduce oxidation, but impair strength under certain conditions.

31. **Godfrey, D. J., and Taylor, P. G., "Inorganic Non-Metallic Bearings, with Special Reference to Silicon Nitride", Special Ceramics, Volume 4, proceedings of the 4th Symposium on Special Ceramics held by the BCRA, Stoke-on-Trent, England, 11-13 July 1967, edited by P. Popper, British Ceramic Research Association, Manchester, England (1968), pp 265-274.**

The problem of reducing friction and wear in hot oxidative or corrosive environments is discussed. The limitations on the use of metallic materials in hot oxidative conditions are considered and the use of inorganic metallic materials for bearings and lubricants is reviewed. Frictional data for Si_3N_4 ceramics are presented, showing they have a potential for use at temperatures at least as high as 700 C.

32. **Godovannaia, I. N., and Popova, O. I., "Oxidation Resistance of Silicon Nitride-Silicon Carbide Refractory Materials at High Temperatures", Chemical Properties and Methods of Analysis of Refractory Compounds, edited by G. V. Samsonov, translated from the Russian by G. D. Archard, Consultants Bureau, New York (1972), pp 33-35.**

Study of the oxidation resistance of Si_3N_4 and SiC refractory materials at temperatures from 1000-1400 C. Results showed the oxidation resistance of these mixed materials to be lower than that of Si_3N_4 or SiC alone.

33. **Goodyear, M. U., and Ezis, A., "Joining of Turbine Engine Ceramics", Advances in Joining Technology, edited by J. J. Burke, A. E. Gorum, and A. Tarpinian, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1977).**

Reaction-sintered and theoretically dense hot-pressed Si_3N_4 materials have been bonded for components for turbine engine applications. Slip-casting techniques for bonding reaction-sintered Si_3N_4 components are discussed as are bonding techniques for hot-pressed Si_3N_4. Results of a bonding parameter study - including bond strength data and interface microstructures - are also presented. The bond between a reaction-sintered blade ring and a hot-pressed hub in a turbine rotor assembly can be as strong as the weaker of the two parent materials.

34. **Goursat, P., Lotholary, P., Tetard, D., and Billy, M., "Silicon Nitride and Oxynitride Stability in Oxygen at High Temperatures", Reactivity of Solids: Proceedings of the Seventh International Symposium on the Reactivity of Solids, Bristol, 17-21 July 1972, edited by J. S. Anderson, M. W. Roberts, and P. S. Stone, Chapman and Hall, London (1972), pp 315-326.**

Kinetics of oxidation of Si_3N_4 and Si_2ON_2 were studied with powdered samples at 1100-1300 C and 0 pressure 15-170 torr. Interfacial and diffusion processes are shown with activation energies, 70 k cal/mole. 0 pressure did not influence the corrosion rate except at the beginning of the reaction.

35. **Grieveson, P., Jack, K. H., and Wild, S., "The Crystal Structures of Alpha and Beta Silicon and Germanium Nitrides", Special Ceramics, Volume 4, proceedings of the 4th Symposium on Special Ceramics held by the BCRA, Stoke-on-Trent, England, 11-13 July 1967, edited by P. Popper, British Ceramic Research Association, Manchester, England (1968), pp 237-238.**

Alpha- and beta-Si_3N_4 are not merely low- and high-temperature forms respectively but are "high oxygen potential" modifications. This explains the anomalies in preparative chemistry of Si_3N_4 and the difficulty of α-β interconversion.

36. **Harris, J. N., "Slip-Cast Sintered Silicon Nitride for Radome Applications", Proceedings of the Twelfth Symposium on Electromagnetic Windows, edited by J. N. Harris, Georgia Institute of Technology, Atlanta (1974), pp 72-75.**

Procedures and results obtained in an experimental study of the suitability of slip-cast reaction-sintered Si_3N_4 for radome applications are described. Results indicate outstanding thermal shock properties and rain erosion resistance superior to fused SiO_2. Remaining development problems are pointed out.

37. **Hayes, C. W., Nessler, C. G., and Zabierek, D., "Turbine Vane Ceramic Endwall", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1975), pp 749-762.**

Preliminary evaluation of hot-pressed Si_3N_4 for ceramic vanes in large aircraft and industrial gas turbines. Prototype vane construction and testing was undertaken with closely related material characterization. Cyclic thermal stress and impact behavior need more attention. Establishing material performance criteria and comparing test data to them is also needed.

38. **Heidemane, G., "Reaction of Aluminum and Silicon with Nitrogen in a Plasma Jet of High Frequency Discharge", Tezisy Dokl.-Konf. Molodykh Nauch. Rab. Inst. Neorg. Khim., Akad Nauk Latv. SSSR, 4th, edited by Yu. N. Sokolov. Riga, Akademuja Nauk Latviiskoi SSR, Institut Neorganicheskoi Khimii, USSR (1975), pp 38-39. (In Russian)**

Changes in the solid reaction product were studied with respect to the axis of the jet, the dependence of the yield of AlN and Si_3N_4 on the size and conditions for the introduction of powdered particles, and on the composition of the high-temperature gas jet for the reaction of Al or Si with N. Highly dispersed powders which contained 10-98% AlN and 5-80% Si_3N_4 were obtained.

39. **Hendry, A., and Jack, K. H., "The Preparation of Silicon Nitride from Silica", Special Ceramics, Volume 6, proceedings of the 6th Symposium on Special Ceramics held by the BCRA, Stoke-on-Trent, England, 9-11 July 1974, edited by P. Popper, British Ceramic Research Association, England (1975), pp 199-208.**

Si_3N_4 was prepared from powder mixtures comprising SiO_2 and C. Discusses conditions for formation of SiC and for varying α/β ratio. SiO overpressure reduces volatilization and favors formation of α-Si_3N_4.

40. **Hendry, A., Perera, D. S., Thompson, D. P., and Jack, K. H., "Phase Relationships in the MgO-Si_3N_4-Al_2O_3 System", Special Ceramics, Volume 6, proceedings of the 6th Symposium on Special Ceramics held by the BCRA, Stoke-on-Trent, England, 9-11 July 1974, edited by P. Popper, British Ceramic Research Association, Manchester, England (1975), pp 321-331.**

β' structures are obtained with the general formula $Mg_{x/4}\ Si_{6-x/4}\ Al_{x/2}\ O_x\ N_{8-x}$. Two new phases were found, both of which are lower symmetry modifications of the hexagonal AlN-type structure; unit cell dimensions and thermal expansion of β' are independent of Mg content.

41. **Henshall, J. L., Rowcliffe, D. J., and Edington, J. W., "The Fracture Toughness and Delayed Fracture of Hot-Pressed Silicon Nitride", Special Ceramics, Volume 6, proceedings of the 6th Symposium on Special Ceramics held by the BCRA, Stoke-on-Trent, England, 9-11 July 1974, edited by P. Popper, British Ceramic Research Association, Manchester, England (1975), pp 185-198.**

Four-point bend tests to determine fracture toughness showed that K_{Ic} varies slightly between 77 and 1273 K, having a minimum value of 4.5 $MN/m^{3/2}$ at room temperature. Above 1273 K, K_{Ic} rises sharply to 10.3 $MN/m^{3/2}$ at 1623 K. In general, fracture is transgranular at 77 K but is intergranular between room temperature and 1273 K. It is suggested that the high K_{Ic} at 1623 K is due to plasticity in the grain boundaries.

42. **Hivert, A., "Elaboration de pointes de radômes en niture de silicium", proceedings of the 3d International Conference on Electromagnetic Windows, Délégation Ministérielle pour l'Armement, Paris, France (1976).**

Fabrication technology of Si_3N_4 radome tips is discussed with emphasis on (1) choice of sintering aids, (2) equipment, and (3) optimum hot-pressing conditions. Bibliography is included.

43. **Jack, K. H., "New Development in Silicon Nitride Ceramics", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1975), pp 265-286.**

The SiO_2 that is always present in Si_3N_4 powders leads to various amounts of extraneous phases in hot-pressed Si_3N_4. The "sialons" - silicon - aluminum oxynitrides - overcome this problem and offer the additional advantage of allowing fabrication by conventional shaping and sintering.

44. **Jama, S.A.B., Thompson, D. P., and Jack, K. H., "The Lithia- Silicon Nitride - Alumina System", Special Ceramics, Volume 6, proceedings of the 6th Symposium on Special Ceramics held by the BCRA, Stoke-on-Trent, England, 9-11 July 1974, edited by P. Popper, British Ceramics Research Association, Manchester, England (1975), pp 299-308.**

Mixtures of title components were formed from various compounds and heated at 1550-1700 C to form β'-structures. Limits of Li_2O solubility in β' are given approximately by the Si_3N_4-$LiAl_5O_8$ join. At higher lithia concentrations phases appear that are isostructural with α-Si_3N_4, Si_2N_2O, and eucryptite. β-structure transforms to α- between 1550 and 1700 C.

45. **Johnson, C. F., and Hartsock, D. L., "Thermal Response of Ceramic Turbine Stator Segments, Stators, and Other Components", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1975), pp 549-562.**

The test facilities used to evaluate Si_3N_4 turbine stators for a regenerative gas turbine engine are described. Thermal response data for various stator vane systems are compared to theoretical values.

46. **Jones, B. F., and Lindley, M. W., "Strength/Density Relationships in Partially Nitrided Silicon Compacts - Their Use in Reaction Sintered Silicon Nitride Research and Technology", Science of Ceramics, Volume 8, British Ceramic Society, Stoke-on-Trent (1976), pp 123-132.**

Important relationships between strength, N weight gain, and nitrided density have been established for reaction-sintered Si_3N_4. Definitive experiments on the deformation and optimization of reaction-sintered Si_3N_4 can now be conducted using these relationships to provide comparisons and assessments. The implications and use of the relationships are explained and discussed.

47. **Kirchner, H. P., and Gruver, R. M., "Fracture Mirrors in Polycrystalline Ceramics and Glass", Fracture Mechanics of Ceramics, Volume 1: Concepts, Flaws, and Fractography, edited by R. C. Bradt, D.P.H. Hasselman, and F. F. Lange, Plenum Press, New York and London (1974), pp 309-321.**

Variations of mirror radius with fracture stress in several materials including hot-pressed Si_3N_4 are compared and evaluated in terms of available theories.

48. **Kossowsky, R., "Creep Fatigue of Si_3N_4 as Related to Microstructure", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1975), pp 347-372.**

High-cycle and low-cycle fatigue, creep, and stress rupture behavior data are presented for hot-pressed Si_3N_4 containing different levels of alkaline impurities, in particular Ca. Results indicate that the strain rate sensitivity of grain boundary sliding determines the temperature and strain rate dependencies of creep and fatigue in Si_3N_4. The effect of impurities on the viscosity of the grain boundary phase is related to the effect of alkaline elements on the creep and stress rupture strength of Si_3N_4.

49. **Kossowsky, R., "Defect Detection in Hot-Pressed Si_3N_4", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1975), pp 665-686.**

X-ray radiography, ultrasonic, and dye penetrant detection techniques were used to identify the types of defects found in commercial hot-pressed Si_3N_4. High density defects such as metallic particles can be detected by X-ray radiography and cavities, low-density areas, and low-density defects by ultrasonic methods. Examples of defect detection in structural components are shown.

50. **Lange, F. F., "Strong, High-Temperature Ceramics", Annual Review of Materials Science, Volume 4, edited by R. A. Huggins, Annual Reviews Inc., Palo Alto, California (1974), pp 365-390.**

A review of SiC and Si_3N_4 as materials being chemically stable at high temperature and possessing those properties necessary for a reliable machine design. Fabrication parameters, microstructures, and properties are emphasized as are structural considerations, thermal-shock resistance, impact strength, and oxidation resistance. Directions for obtaining improved and new materials are discussed.

51. **Lange, F. F., and Iskoe, J. L., "High-Temperature Strength Behavior of Hot-Pressed Si_3N_4 and SiC: Effects of Impurities", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1975), pp 223-238.**

Subcritical crack growth in hot-pressed Si_3N_4 occurs by grain boundary sliding. Ca impurity in the glassy grain boundary phase severely decreases high temperature strength while Fe and Al have no apparent effect. Typical high purity of SiC powders (compared to Si_3N_4) may explain reduced susceptibility of hot-pressed SiC to subcritical crack growth.

52. **Lenoe, E. M., "Probability Based Design and Analysis - The Reliability Problem", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1975), pp 123-146.**

The general problem of engine reliability is reviewed. Statistical models for strength and modulus for hot-pressed Si_3N_4 with regard to ceramic engine applications are discussed. A specific example is given of probability of failure computations for deterministic mechanical and thermal stresses in the first-stage rotor of the vehicular engine project.

53. **Lenoe, E. M., and Quinn, G. D., "Preliminary Creep Studies of Hot-Pressed Silicon Nitride", Deformation of Ceramic Materials, edited by R. C. Bradt and R. E. Tressler, Plenum Press, New York (1975), pp 399-412.**

Review of the literature concerning creep behavior of Si_3N_4. Preliminary observations of the tension and torsion response of hot-pressed Si_3N_4 are also reported. Tension response was explored for stresses up to 3500 psi and torsion behavior for up to 7400 psi. Shear deformation appeared to occur at fairly low stress levels and the initial and short-time creep strain rate was $\sim 6.1 \times 10^{-4}$ in/in-hr.

54. **Lindley, M. W., and Katz, R. N., "High Temperature Engineering Ceramic (Si_3N_4) by Powder Metallurgy", Powder Metallurgy for High Temperature Applications, proceedings of the 18th Sagamore Army Materials Conference, Racquette Lake, New York, September 1971, edited by J. J. Burke and V. Weiss, Syracuse University Press, Syracuse, New York (1972), pp 375-380.**

A brief review of the preparation and properties of reaction-sintered Si_3N_4.

55. **Lines, D. J., "Ceramic Materials for Gas Turbine Components", High-Temperature Materials in Gas Turbines, edited by P. R. Sahm and M. O. Speidel, Elsevier Scientific Publishing Company, Amsterdam and New York (1974), pp 155-186.**

Review of potential advantages and disadvantages of the use of ceramic materials in gas turbine engines. The physical properties and fabrication techniques for six basic forms of Si_3N_4 and SiC are also reviewed.

56. **Lloyd, D. E., "High-Temperature Properties of Reaction-Sintered and Hot-Pressed Silicon Nitride and Their Relation to Fabrication Conditions", Special Ceramics, Volume 4, proceedings of the 4th Symposium on Special Ceramics held by the BCRA, Stoke-on-Trent, England, 11-13 July 1967. Edited by P. Popper, British Ceramic Research Association, Manchester, England (1968), pp 165-172.**

Hot pressing or reaction sintering is usually used to fabricate Si_3N_4 into usable bodies. The properties of the two forms differ markedly at room temperature and at elevated temperatures. Results of some mechanical properties, modulus of rupture, elasticity, and impact strength, at elevated temperature are described. The influence of fabrication conditions on the retention of strength at high temperatures is mentioned.

57. **Lumby, R. J., North, B., and Taylor, A. J., "Chemistry and Creep of Sialons", Special Ceramics, Volume 6, proceedings of the 6th Symposium on Special Ceramics held by the BCRA, Stoke-on-Trent, England, 9-11 July 1974, edited by P. Popper, British Ceramic Research Association, Manchester, England (1975), pp 283-298.**

The chemistry of sialons is discussed in relation to the degree of O and Al substitution. Reasons are suggested for multiphase products of reactions between Si_3N_4 and Al_2O_3. Properties are given for materials prepared from Si_3N_4, AlN, and SiO_2. Suggest $Si_{6-z}\,Al_z\,N_{8-z}\,O_z$ formula for expanded β-Si_3N_4 structure.

58. **Mangels, J. A., "Development of a Creep Resistant Reaction Sintered Si_3N_4", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1975), pp 195-206.**

Bend testing was used to investigate creep of injection molded reaction-sintered Si_3N_4 and effects of impurity levels and nitriding atmospheres on the creep rate were evaluated. Creep rates and creep strains were decreased by reducing the Ca impurity level and by nitriding in a H environment. Test samples were analyzed by scanning electron microscopy and grain boundaries by Auger spectroscopy.

59. **Marquis, P. M., and Long, N. J., "High Voltage Microscopy Studies of Planar Interfaces in Reaction Sintered Silicon Nitride", High Voltage Electron Microscopy, edited by P. R. Swann, Academic Press, New York and London (1973), pp 260-263.**

The planar growth faults of reaction-sintered Si_3N_4 were investigated. The structure and nature of three planar interfaces are described.

60. **McLean, A. F., "Ceramics in Small Vehicular Gas Turbines", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1975), pp 9-36.**

Overview of progress on program aimed at the application of ceramics to small vehicular gas turbine.

61. **Messier, D. R., and Wong, P., "Kinetics of Formation and Mechanical Properties of Reaction Sintered Si_3N_4", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1975), pp 181-194.**

Considers effects of Si particle size and purity on strength of reaction-sintered Si_3N_4. Purity had no effect while strength was enhanced by fine particle size (-400 mesh) and low maximum firing temperature (1400 C). Strength controlling defects appeared to be "meltout" pores.

62. **Messier, D. R., and Wong, P., "Silicon Nitride: A Promising Material for Radome Applications", Proceedings of the Twelfth Symposium on Electromagnetic Windows, edited by J. N. Harris, Georgia Institute of Technology, Atlanta, Georgia (1974), pp 62-66.**

Dielectric properties of reaction-sintered and hot-pressed Si_3N_4 are dependent upon extraneous phases, particularly unreacted Si. Data are given for eight Si_3N_4 materials.

63. **Metcalfe, A. G., "Application of Ceramics to Radial Flow Gas Turbines at Solar", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1975), pp 739-748.**

Use of ceramic nozzle guide vanes and shrouds considered for small radial flow gas turbines. Tests indicated feasibility of this approach.

64. **Nessler, C. G., "Evaluation of Prototype Vanes", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1975). pp 609-632.**

Describes program on fabrication and testing of hot-pressed Si_3N_4 gas turbine vane platform (endwall).

65. **Noakes, P. B., and Pratt, P. L., "High-Temperature Mechanical Properties of Reaction-Sintered Silicon Nitride", Special Ceramics, Volume 5, proceedings of the 5th International Symposium on Special Ceramics held by the BCRA, Stoke-on-Trent, England, 14-16 July 1970, edited by P. Popper, British Ceramic Research Association, Manchester, England (1972), pp 299-310.**

The modulus of rupture and the modulus of elasticity of reaction-sintered Si_3N_4 were determined between room temperature and 1500 C. The relationship between these properties and the isostatic pressing pressure of the Si powder was investigated. The micro-identation hardness of the α- and β-Si_3N_4, Si, and SiC phases in impure Si_3N_4 was determined.

66. **Oliver, D. A., "Silicon Nitride: A Review of Its Properties and Attractiveness for Use at Elevated Temperatures", High Temperatures in Aeronautics, proceedings of the Symposium held in Turin to celebrate the 50th anniversary of the Laboratorio di aeronautica, Potitecnico di Torino, 10-12 September 1962, edited by Carlo Ferrari, Pergamon Press, New York and Oxford (1964), pp 377-384.**

The manufacture of Si_3N_4 and its influence on the density of the product, the high thermal-shock resistance and its relation to the low coefficient of thermal expansion, the mechanical properties, and possible applications of Si_3N_4 are discussed.

67. **Parr, N. L., Martin, G. F., and May, E.R.W., "Preparation, Microstructure, and Mechanical Properties of Silicon Nitride", Special Ceramics, edited by P. Popper, Academic Press, New York (1960), pp 102-135.**

Si_3N_4, although brittle at room temperature, has excellent oxidation resistance, good thermal shock resistance, and adequate creep strength at temperatures up to 1200 C if stiffened with a very fine dispersion of SiC. Methods for producing the material in suitable form and in the best physical state for engineering designs have been fully explored by laboratory evaluation and field trials. Some applications are described and others suggested.

68. **Perry, G. S., and Moules, T. R., "Microwave Dielectric Properties of Silicon Nitrides", Proceedings of the Twelfth Symposium on Electromagnetic Windows, edited by J. N. Harris, Georgia Institute of Technology, Atlanta, Georgia (1974), pp 67-71.**

Results of microwave high temperature dielectric measurements combined with chemical, X-ray, micrographic, and other physical property investigations, performed on a variety of Si_3N_4 ceramics are reviewed. Si_3N_4 combines low dielectric loss with a low-temperatures coefficient of permittivity, both of which are desirable for radomes.

69. **Petrovic, J. J., and Jacobson, L. A., "The Strength of Silicon Nitride After Exposure to Different Environments", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1975), pp 397-414.**

Room temperature fracture strength of 25 specimens of commercial hot-pressed Si_3N_4 was determined in four-point bending. Fracture strength was found to increase after exposure at temperatures >1173 K, relatively independent of the exposure environment. Strength increase is attributed to decrease of stress at crack tip resulting from localized plastic deformation. High fracture energy values on specimens annealed at >1500 K were close to values (39 J/m^2) obtained by other investigators.

70. **Pratt, P. L., "The Microstructure and Mechanical Properties of Silicon Nitride", Mechanical Properties of Engineering Ceramics, edited by W. Wurth Kriegel and Hayne Palmour III, Interscience Publishers, New York (1961), pp 507-519.**

Studies of the microstructure of reaction-sintered Si_3N_4 reveal the presence of a number of phases which may be distinguished by their micro-hardness properties. The phases are identified by X-ray methods, and their relative proportions and distribution are considered in terms of the bulk density of material prepared in a number of ways. The influence of this microstructure upon the mechanical properties is indicated and some explanation of the good thermal shock resistance is given.

71. **Rae, A.W.J.M., Thompson, D. P., Pipkin, N. J., and Jack, K. H., "The Structure of Yttrium Silicon Oxynitride and Its Role in the Hot-Pressing of Silicon Nitride With Yttria Additions", Special Ceramics, Volume 6, proceedings of the 6th Symposium on Special Ceramics held by the BCRA, Stoke-on-Trent, England, 9-11 July 1974, edited by P. Popper, British Ceramic Research Association, Manchester, England (1975), pp 347-360.**

There is no appreciable solubility of Y_2O_3 in Si_3N_4. Principal phases in hot-pressed material are β-Si_3N_4 and tetragonal $Y_2Si_3O_3N_4$. Also identified were two intermediate phases that occur between 1000 and 1300 C. $Y_2Si_3O_3N_4$ accomodates impurities such as Ca; formation of low-melting glasses is thus avoided and Y_2O_3-Si_3N_4 hot-pressed material has high hot strength.

72. **Rao, B. V., and Tamhankar, R. V., "Silicon Nitride", High Temperature Materials, proceedings of the 3d Symposium on Materials Science Research, Hyderabad, India, 21-23 February 1972, Department of Atomic Energy, Government of India, Bombay (1973), pp 125-145. (In English)**

A review of the methods for fabrication of and improvement of engineering properties of Si_3N_4 refractories. Design of components made of this material is also included.

73. **Sanders, W. A., and Probst, H. B., "High-Gas-Velocity Burner Tests of Silicon Carbide and Silicon Nitride at 1200 C", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1975), pp 493-532.**

Ten SiC and five Si_3N_4 materials were exposed in a Mach 1 gas-velocity burner and cycle tested for up to 100 hours at 1200 C. One hot-pressed SiC, one reaction-sintered SiC, and three hot-pressed Si_3N_4 materials survived 100 one-hour cycle exposures. The other materials failed from thermal fatigue.

74. **Seydel, J. A., "Improved Discontinuity Detection in Ceramic Materials Using Computer-Aided Ultrasonic Nondestructive Techniques", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1975), pp 697-710.**

Results on hot-pressed Si_3N_4 test samples inspected with a conventional ultrasonic system were compared with those obtained with a computer-aided ultrasonic system. Test sensitivity and test resolution were improved using three data processing techniques.

75. **Singhal, S. C., "Oxidation and Corrosion-Erosion of Si_3N_4 and SiC", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1975), pp 533-548.**

Corrosion of hot-pressed Si_3N_4 and SiC were studied by static oxidation and also by corrosion-erosion tests in a pressurized turbine test passage. Static oxidation was parabolic for both materials at 1000-1400 C with impurities greatly influencing the composition of the oxide layer. Although both materials showed erosion in the dynamic tests at 1100 C, their strengths were unaffected by the gas turbine environment.

76. **Styhr, K. H., "Spin Testing of Ceramic Turbine Rotors", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1975), pp 415-424.**

Cold-spin testing of Si_3N_4 "multidensity" rotors has been used for evaluation and for identification of failure conditions. A wide range of failure conditions have been identified during the testing phase allowing for the development of improved rotors suitable for subsequent hot testing and engine development.

77. **Thompson, D. S., and Pratt, P. L., "The Structure of Silicon Nitride", Science of Ceramics, Volume 3, proceedings of the 3d Conference of the British Ceramic Society and the Nederlandse Keramische Vereniging held under the auspices of the European Ceramic Association at the University of Bristol, 5-8 July 1965. Edited by G. H. Stewart, Academic Press, New York (1967), pp 33-51.**

A detailed analysis of the crystal structure of β-Si_3N_4 has been made, together with a partial analysis of the α-phase. Models of both have been made revealing the features of certain crystallographic planes. Some studies of the transformation from α- to β-Si_3N_4 at high temperatures have been made. The effect of temperature on the lattice parameters of Si_3N_4 has been studied using a high-temperature X-ray camera. The microstructure of reaction-sintered Si_3N_4 appears to consist of dense grains in a sea of interconnected flakes. Nitriding at temperatures above the melting point of Si leads to the growth of largely β-Si_3N_4 with only small amounts of α.

78. **Thuemmler, F., Porz, F., Grathwohl, G., and Engel, W., "Kriechen und Oxidation von Reaktionsgesintertem Si_3N_4", Science of Ceramics, Volume 8, British Ceramic Society, Stoke-on-Trent, England (1976), pp 133-144.**

Creep tests in four-point bending performed on reaction-sintered Si_3N_4 in air and in vacuum at temperatures up to 1400 C. Creep deformations were very much smaller in vacuum than in air because of the formation of O-containing phases in the oxidizing atmospheres. Concentration profiles were obtained by X-ray analysis. Internal oxidation may be restricted in several ways.

79. **Tighe, N. J., "Examination of Fracture Interfaces in Silicon Nitride", Proceedings of the Thirty-Third Annual Meeting of the Electron Microscope Society of America, edited by G. W. Bailey, Claitor's Publishing Division, Baton Rouge, Louisiana (1975), pp 60-61.**

Fracture is mostly intergranular and oxidation occurs after fracture. Photomicrographs illustrate fracture phenomena.

80. **Tighe, N. J., "Microstructure of Oxidized Silicon Nitride", Proceedings of the Thirty-Second Annual Meeting of the Electron Microscope Society of America, edited by C. J. Arceneaux, Claitor's Publishing Division, Baton Rouge, Louisiana (1974), pp 470-471.**

Thin foil and bulk Si_3N_4 samples were oxidized in air 1000, 1200, or 1400 C for 1-264 hours, and the oxidation products ($SiON_2$, β-SiO_2) and two amorphous phases were studied by electron microscopy using specimens prepared by ion thinning. Oxidation of the Si_3N_4 grains started at the grain boundaries.

81. **Torre, J. P., and Mocellin, A., "On the Existence of Si-Al-O-N Solid Solutions Based on Al_2O_3 Transition Structures", Special Ceramics, Volume 6, proceedings of the 6th symposium on Special Ceramics held by the BCRA, Stoke-on-Trent, England, 9-11 July 1974, edited by P. Popper, British Ceramic Research Association, Manchester, England (1975), pp 333-345.**

Study on diffusion couples comprising α-Si_3N_4 and α-Al_2O_3 revealed new quaternary phase resembling γ- or δ-type Al oxides or oxynitrides. Unit cell of new phase is orthorhombic.

82. **Torti, M. L., Alliegro, R. A., Richerson, D. W., Washburn, M. E., and Weaver, G. Q., "High-Temperature Properties of Silicon Carbide and Silicon Nitride", High-Temperature Materials in Gas Turbines, edited by P. R. Sahm and M. O. Speidel, Elsevier Technical Publishing Company, Amsterdam and New York (1974), pp 177-186.**

Room- and high-temperature properties of hot-pressed and reaction-sintered Si_3N_4 are listed and compared. Properties reviewed include density, elastic modulus, thermal expansion, tensile and bend strength, creep, oxidation and stress-rupture life.

83. **VanBuren, W., Schaller, R. J., and Visser, C., "Stress Analysis of a Ceramic Rotor Design Subjected to Centrifugal and Thermal Loads", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1975), pp 157-178.**

A 3-D finite element stress analysis of a proposed ceramic rotor blade design is presented. Design considerations include thermal and centrifugal loading conditions. Also obtained were natural frequencies of the airfoil portion of the blade.

84. **Walton, J. D., Jr., "Reaction Sintered Silicon Nitride as a Hypersonic Radome Material", Proceedings of the Eleventh Symposium on Electromagnetic Windows, edited by N. E. Poulos and J. D. Walton, Jr., Georgia Institute of Technology, Atlanta, Georgia (1972), pp 103-106.**

The dielectric, thermal shock, and erosion properties of reaction-sintered Si_3N_4 appear attractive for use in radomes at high-flight velocities. Fabrication techniques are also considered.

85. **Walton, J. D., Jr., "State of Hypersonic Radome Technology Slip-Cast Fused Silica and Reaction Sintered Silicon Nitride", Proceedings of the 3d International Conference on Electromagnetic Windows, Volume 1, Délégation Ministérielle pour l'Armement, Paris, France (1976), pp 381-393, 395, 397-400.**

Collection of pertinent electrical, mechanical, and thermal property data for the hypersonic radome materials - slip-cast fused silica and reaction-sintered Si_3N_4. Effects of temperature and porosity are considered, and thermal shock and rain erosion are discussed in relation to porosity.

86. **Washburn, M. E., and Baumgartner, H. R., "High-Temperature Properties of Reaction-Bonded Silicon Nitride", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1975), pp 479-492.**

Data are presented for high-strength reaction-bonded Si_3N_4. Included are oxidation behavior in air at 1200 and 1375 C and flexural strength values from ambient to 1450 C. Flexural strength was >50,000 psi at 1450 C and no creep deformation occurred in 260 hours at 2260 C under a load of 20,000 psi.

87. **Waugh, J. S., and Goldstein, S. D., "A Rain Erosion Evaluation of Three Dimensional Woven Silica and Reaction Sintered Silicon Nitride as State-of-the-Art Radome Materials", Proceedings of the Twelfth Symposium on Electromagnetic Windows, eidted by J. N. Harris, Georgia Institute of Technology, Atlanta, Georgia (1974), pp 128-132.**

Rain erosion resistance of Si_3N_4 appears adequate for radome applications.

88. **Weaver, G. Q., Baumgartner, H. R., and Torti, M. L., "Thermal Shock Behavior of Sintered Silicon Carbide and Reaction-Bonded Silicon Nitride", Special Ceramics, Volume 6, proceedings of the 6th Symposium on Special Ceramics held by the BCRA, Stoke-on-Trent, England, 9-11 July 1974, edited by P. Popper, British Ceramic Research Association, Manchester, England (1975), pp 261-281.**

Si_3N_4 materials tested had ΔT critical of about 400 C versus 300-375 C for SiC. Residual strength of the better SiC was twice that of the Si_3N_4.

89. **Wild, S., "A Preliminary Investigation of the Reaction of Alpha-Silicon Nitride With Metakaolin", Special Ceramics, Voluem 6, proceedings of the 6th Symposium on Special Ceramics held by the BCRA, Stoke-on-Trent, England, 9-11 July 1974, edited by P. Popper, British Ceramics Research Association, Manchester, England (1975), pp 309-320.**

Reaction formed new phase designated "X" that decomposes in two stages to form an aluminum oxynitride analog and, finally, α-Al_2O_3. "X" phase appears to be a quaternary phase in the system Si-Al-N-O.

90. **Wild, S., Grieveson, P., and Jack, K. H., "The Crystal Chemistry of New Metal-Silicon-Nitrogen Ceramic Phases", Special Ceramics, Volume 5, proceedings of the 5th International Symposium on Special Ceramics held by the BCRA, Stoke-on-Trent, England, 14-16 July 1970, edited by P. Popper, British Ceramic Research Association, Manchester, England (1972), pp 289-298.**

The possible importance of ternary and quaternary phases and of related materials in Si_3N_4 technology is discussed.

91. **Wild, S., Grieveson, P., and Jack, K. H., "The Crystal Structures of Alpha and Beta Silicon and Germanium Nitrides", Special Ceramics, Volume 5, proceedings of the 5th International Symposium on Special Ceramics held by the BCRA, Stoke-on-Trent, England, 14-16 July 1970, edited by P. Popper, British Ceramic Research Association, Manchester, England (1972), pp 385-396.**

The crystal structures of α- and β-Ge_3N_4 and α-Si_3N_4 were determined by X-ray powder methods and accurate atomic parameters were obtained. The parameters of β-Si_3N_4 agreed with previous determinations. Structural data shows that the α- "nitrides" are in fact oxynitrides with O replacing N in some sites and with N vacancies in others. α- and β- are not merely low-temperature and high-temperature structural forms of the same compound, but are "high oxygen potential" and "low-oxygen potential" modifications.

92. **Wild, S., Grieveson, P., and Jack, K. H., "Thermodynamic and Phase Relations in the Silicon-Nitrogen-Oxygen System", Metallurgical Chemistry, Proceedings of a Symposium, 1971, edited by O. Kubaschewski, Her Majesty's Stationery Office, London, England (1972), pp 339-346.**

α-Si_3N_4 has a defect structure containing 0 atoms as well as vacant lattice sites. α- and β-Si_3N_4 are not merely low- and high-temperature forms. Phase relations α- and β-Si_3N_4, Si_2N_2O, and Si are discussed.

93. **Wild, S., Grieveson, P., and Jack, K. H., "The Thermodynamics and Kinetics of Formation of Phases in the Ge-N-O and Si-N-O Systems", Special Ceramics, Volume 5, proceedings of the 5th International Symposium on Special Ceramics held by the BCRA, Stoke-on-Trent, England, edited by P. Popper, British Ceramic Research Association, Manchester, England (1972), pp 271-288.**

The thermodynamic conditions for the formation of α- "high-oxygen potential" and β- "low-oxygen potential" Si_3N_4 from Si have been established over a wide range of temperatures. Kinetic factors and the O "capacity" of the environment are equally important in determining the α:β ratio. In reaction with pure Si, α- is formed by a vapour-phase reaction. When β- is produced as a coherent layer on the metal surface, further reaction is retarded because of slow diffusion through the Si_3N_4. β-Si_3N_4 can be obtained by the equilibration of Si in Si-Fe alloys with appropriate N and O potentials at temperatures as low as 550 C, invalidating previous claims that it is a high-temperature phase.

94. **Wild, S., Grieveson, P., Jack, K. H., and Latimer, M. J., "The Role of Magnesia in Hot-Pressed Silicon Nitride", Special Ceramics, Volume 5, proceedings of the 5th International Symposium on Special Ceramics held by the BCRA, Stoke-on-Trent, England, edited by P. Popper, British Ceramic Research Association, Manchester, England (1972), pp 377-384.**

X-ray studies were made of Si_3N_4 powders with various additions of MgO hot-pressed for 1 hour over a wide range of temperatures. At low temperatures, 100-1400 C, the MgO is converted to forsterite (Mg_2SiO_4). At higher temperatures the forsterite reacts with α-Si_3N_4 to produce enstatite ($MgSiO_3$) and β-Si_3N_4. Maximum changes as rapid densification, disappearance of forsterite, decrease in α:β ratio, and increase in strength, all occur at about 1557 C, the melting point of enstatite. That the enstatite phase acts as a bond between the Si_3N_4 particles explains the low high-temperature strength of hot-pressed Si_3N_4.

95. **Airey, A. C., Clarke, S., and Popper, P., "Pyrolytic Silicon Nitride Coatings", Proc. Brit. Ceram. Soc., No. 22, 305-320 (1973).**

Amorphous α-Si_3N_4 coatings were directly deposited with SiH_4/NH_3 but with $SiCl_4/NH_3$ both amorphous and crystalline α-Si_3N_4 coatings were obtained. Coatings deposited above 900 C were similar to Si_3N_4 composition, those below 900 C contained excess Si, all contained small amount of O. All amorphous coatings were cracked but the extent of cracking decreased with increasing deposition temperature and density.

96. **Akio, K., Yoshihro, O., Sanae, K., and Isao, M., Yogyo Kyohai Shi, 80 (3), 28-34 (1972). (See Entry No. 409)**

97. **Alliegro, R. A., and Torti, M. L., "Ceramics--Key to the 'Hot' Turbine", Gas Turbine Int., 30-36 (January-February 1973).**

Discussion of the problems that must be overcome, primarily stress concentrations, in ceramic materials before they can be successfully used in gas turbine engines. Reviews the physical properties - density, elastic modulus, coefficient of thermal expansion, thermal conductivity, and specific heat - of four potential materials including hot-pressed and reaction-bonded Si_3N_4 and SiC.

98. **Amato, I., Martorana, D., and Rossi, M., "Nitriding of Silicon Powder Compacts", Powder Met., 18, 339-348 (1975).**

Report of the influences of raw materials and processing variables on the preparation of Si_3N_4 by reaction bonding. Gas permeation was rate-limiting and the degree of nitridation increased with temperature from 1300-1400 C. Oxygen impurities enhance formation of α-Si_3N_4.

99. **Ammann, C. L., Doherty, J. E., and Nessler, C. G., "The Thermal Fatigue Behavior of Hot Pressed Silicon Nitride", Mater. Sci. Eng., 22, 15-22 (1976).**

Cyclic fluidized-bed quenching was used to evaluate the thermal fatigue resistance of hot-pressed Si_3N_4. Finite element analysis showed that behavior of wedge-shaped specimens simulated that of turbine vane. Thermal fatigue can limit the application of hot-pressed Si_3N_4 in transient high-temperature environments. When analyzed in terms of slow crack growth mechanisms, thermal fatigue life is sensitive to strain level and duration above 1000 C.

100. **Ashcroft, W., "Mechanical Properties of Silicon Nitride at Elevated Temperatures", Proc. Brit. Ceram. Soc., No. 22, 169-179 (1973).**

Work on the strength of hot-pressed and flame-sprayed reaction-sintered commercial types of Si_3N_4 is described. Variation in the rupture modulus and elastic modulus at temperatures from 30-1450 C are described. The plasticity of hot-pressed Si_3N_4 at temperatures 1200 C and above are also described. Initial results on the delayed fracture of hot-pressed Si_3N_4 are presented. A brief account of high-temperature creep is included.

101. **Atkins, A. G., and Tabor, D., "Hardness and Deformation Properties of Solids at Very High Temperatures", Proc. Roy. Soc., London Ser. A, 292, 441-459 (1966).**

Indentation hardness of refractory borides, carbides, and nitrides was determined at temperatures up to 2000 C. Most of the refractory solids are very brittle at low temperatures. Above a critical temperature (half absolute melting point) they become ductile and the hardness falls as the temperature increases. Si_3N_4 and SiC are the only materials having an indentation hardness above 100 kg/mm^2 at 1500 C.

102. **Atkinson, A., and Evans, A. D., "Temperature Gradients in Nitriding Silicon Powder Compacts", Brit. Ceram. Soc. Trans. J., 73, 43-46 (1974).**

Temperature distributions occurring in Si_3N_4 powder compacts, 5 cm diam x 5 cm long, were measured as a function of time during nitridation at temperatures from 1295 to 1330 C. The temperature distributions were shown to be determined by a rise in surface temperature allowing heat to be radiated and the establishment of a temperature gradient.

103. **Atkinson, A., Leatt, P. J., and Moulson, A. J., "The Nitriding of Silicon Powder Compacts", J. Mater. Sci., 7, 482-484 (1972).**

Results of nitriding of Si powder compacts containing up to 50 w/o Si_3N_4 indicate that gas diffusion is the rate-determining step. Additions of Al to the Si compacts increased nitridation rate and amount of β-Si_3N_4 formed at 1350 C.

104. **Atkinson, A. Leatt, P. J., and Moulson, A. J., "The Role of Nitrogen Flow into the Nitriding Compact in the Production of Reaction-Sintered Silicon Nitride", Proc. Brit. Ceram. Soc., No. 22, 253-274 (1973).**

Results of a study to determine to what extent N flow into the compact controls the overall reaction rate during the nitriding of Si powders. The reaction rate was measured using thermogravimetry as a function of compact pore structure, Si particle size, compact (spherical) size, up to 5 cm diameter, and reaction temperature. Evidence points to the reaction between Si and N and not the rate of flow of N into the compact as being the rate-determining step.

105. **Atkinson, A., Leatt, P. J., Moulson, A. J., and Roberts, E. W., "A Mechanism for the Nitridation of Silicon Powder Compacts", J. Mater. Sci., 9, 981-984 (1974).**

A mechanism is proposed for the nitridation of Si powder based on the untypical microstructure of a partially nitrided Si compact. Microstructural examination shows that nitridation does not occur at the Si-Si_3N_4 interface but that it proceeds via a pore migration mechanism.

106. **Atkinson, A., Moulson, A. J., and Roberts, E. W., "Nitridation of High-Purity Silicon", J. Mater. Sci., 10, 1242-1243 (1975).**

Growth and morphology of Si_3N_4 on high-purity Si indicate that the process involves vapor-phase transport and/or surface diffusion rather than solid state diffusion.

107. **Atkinson, A., Moulson, A. J., and Roberts, E. W., "Nitridation of High Purity Silicon", J. Amer. Ceram. Soc., 59, 285-288 (1976).**

A model is presented to explain kinetic data for the nitridation of pure Si at 1250-1370 C and N pressures of 20-760 torr. The initial linear kinetics are associated with the growth of individual nitride nuclei. The reaction rate steadily decreases as the nuclei coalesce and falls to zero when the Si is completely covered with nitride.

108. **Batha, H. D., and Whitney, E. D., "Kinetics and Mechanism of the Thermal Decomposition of Si_3N_4", J. Amer. Ceram. Soc., 56, 365-369 (1973).**

Using a static system the kinetics of the thermal decomposition of Si_3N_4 were studied. At 1400-1750 C, Si_3N_4 decomposed to liquid Si and N gas, following first-order kinetics during the initial stages of dissociation and the Jander solid-state kinetic law in the latter stages. The activation energies for the first-order and Jander kinetics were 93.0 ± 6.6 kcal mol^{-1} and 186 ± 10 kcal mol^{-1} respectively. Excess Si metal and a N atmosphere in the reaction system inhibited the decomposition reaction.

109. **Billy, M., "Preparation and Definition of Silicon Nitride", Ann. Chim. (Paris), 4, 795-851 (1959). (In French)**

The reaction of Si and N at high temperatures produced only the nitride Si_3N_4. Si and N begin to react at temperatures above 1240 C. The reaction is slow between 1250 and 1315 C. Between 1315 and 1385 C, a logarithmic rate law obtains. Above 1385 C, the rate of reaction is very rapid. The crystal structure of Si_3N_4 is orthorhombic.

110. **Billy, M., Brossard, M., Desmaison, J., Giraud, D., and Goursat, P., "Synthesis of Si and Ge Nitrides and Si Oxynitride by Ammonolysis of Chlorides - Comment on 'Synthesis Characterization and Consolidation of Si_3N_4 Obtained from Ammonolysis of $SiCl_4$' ", J. Amer. Ceram. Soc., 58, 254-255 (1975).**

Comment on paper by Mazdizasni and Cooke with reply by those authors. Papers deal with chemistry of title systems.

111. **Birch, J. M., Wilshire, B., Owen, D.J.R., and Shantaram, D., "The Influence of Stress Distribution on the Deformation and Fracture Behavior of Ceramic Materials Under Compression Creep Conditions", J. Mater. Sci., 11, 1817-1825 (1976).**

Finite element method was used to determine stress distribution that developed in test pieces of reaction-bonded Si_3N_4 during compression. The accommodation of grain-boundry sliding by cavity formation appears to be the rate-controlling process during high-temperature creep.

112. **Blake, M., "New, Improved Silicon Nitride Vies for High Performance Bearings", Mater. Eng., 78, 30-32 (1973).**

Discusses the performance of hot-pressed Si_3N_4 in bearing applications.

113. **Borgen, O., and Seip, H. M., "The Crystal Structure of β-Si_3N_4", Acta Chem. Scand., 15, 1789 (1961).**

The crystal structure of β-Si_3N_4 was reinvestigated using X-ray intensities measured photometrically from integrated Weissenberg films. The space group and unit cell parameters found by earlier investigators were reaffirmed.

114. **Brachet, D., Goursat, P., and Billy, M., "Mise en évidence d' une nouvelle phase quaternaire du système Si-Al-O-N", C. R. Herbd. Seances Acad. Sci., Ser. C, 280, 1207-1209 (1975).**

The new phase $SiAl_4N_4O_2$ was prepared by heating mixures of Si_2ON_2 and Al_2O_3 in Ar atmosphere at 1650-1700 C. It is regarded as the thermolysis product of the solid solution β' -Si_3N_4.

115. **Brennan, J. J., and Novak, R. C., "The Effect of the Interface on the Impact Strength of Fiber-Reinforced Silicon Nitride Composites", J. Adhes., 5, 139-159 (1973).**

The addition of 30 v/o W wires to hot-pressed Si_3N_4 increased the Charpy impact strength at 1300 C from 0.25 ft-lbs to 2.25 ft-lbs. At this temperature the interfacial shear strength is low enough to allow the energy absorbing mechanism of fiber pullout to be operative. At room temperature,however, the tungsten silicide layer formed at the W-Si_3N_4 interface rendered W reinforcement ineffective. Means of solving this problem are discussed.

116. **Brokhin, I. S., and Funke, V. F., "The Preparation of Silicon Nitride and the Investigation of Some of its Properties", Ogneupory, 22, 562-566 (1957). (In Russian)**

Lists the physical and chemical properties of Si_3N_4. In the nitriding process the Si should be powdered to a fineness of at least 40 μm. Formation of Si_3N_4 begins at 970 C; the rate of formation reaches a maximum at 1600 C and drops sharply above 1700 C. Metallic impurities are eliminated by boiling in a 50% solution of HCl. Data on the influence of the nitriding temperature and the concentration of N are shown.

117. **Brown, R. L., "The Flame Sprayed Deposition of Silicon Powder for the Production of Silicon Nitride Ceramics", Metal Construction Brit. Weld. J., 1, 317-321 (1969).**

Porous Si forms prepared by flame-spray deposition of Si powder were nitrided to produce Si_3N_4 bodies. This method provides for economic production of accurate and intricate shapes of Si_3N_4.

118. **Burykina, A. L., and Kosteruk, V. P., "Influence of Ambient Atmosphere on the Reaction of Silicon Nitride With Titanium", Sov. Powder Met. Metal Ceram., 12, 983-987 (1973). Translation of Porosh. Met., No. 12, 49-54 (1973).**

Concludes from experiments and thermodynamic analysis that Si_3N_4 should not be used as electrical insulator in contact with Ti at temperatures $>$1200 C.

119. **Butler, E., "Observations of Dislocations in β-Silicon Nitride", Phil. Mag., 24, 829-834 (1971).**

Dislocations in β-Si_3N_4 generated by fracture at room temperature were examined by transmission electron microscopy. The dislocations lie on [1010] and are near edge orientation with Burgers Vector c[0001].

120. **Campos-Loriz, D., "Silicon Nitride and Similar Materials", Ind. Minera (Madrid), 18 (163), 19,21,23,25,27-28 (1976). (In Spanish)**

A review with 16 references.

121. **Campos-Loriz, D., and Riley, F. L., "The Effect of Silica on the Nitridation of Silicon", J. Mater. Sci., 11, 195-198 (1976).**

Effects of alumina refractories on nitridation are discussed. Formation of α-Si_3N_4 is related to presence of SiO_2 in compact being nitrided. Role of metallic impurities in nitridation is also considered.

122. **Cappelli, P. G., "Ceramic Materials for Engineering Applications: Silicon Nitride", Met. Ital., 67, 248-254 (1975). (In Italian)**

Reaction-sintering and hot-pressing techniques for the manufacture of Si_3N_4 components are discussed. Reaction sintering is best carried out at 1300-1400 C for 40 hours using fine Si powder containing some Fe. Hot pressing should be done at 1650 C for 60 minutes at 500 kg/cm^2.

123. **"Ceramics Based on Silicon Nitride", Nature, 238, 128-129 (July 21, 1972).**

Review of development and properties of Si_3N_4 for structural applications and discussion of modified materials having β-Si_3N_4 structure.

124. **"Ceramics Come in from the Cold with New Uses", The Engineer, 243, 56-58 (July 22, 1976).**

Review of Advanced Materials Engineering's work with reaction-bonded Si_3N_4 in automotive applications such as diesel pistons and turbocharger impellers.

125. **Chen, E. P., and Hasselman, D.P.H., "Comparison of the High-Temperature Thermal Fatigue Resistance of Hot-Pressed Silicon Nitride and Silicon Carbide", J. Amer. Ceram. Soc., 59, 525-526 (1976).**

Calculations indicate that Si_3N_4 can withstand higher temperatures than SiC for short thermal fatigue life under certain conditions, but also that SiC is superior for long-term thermal fatigue.

126. **Clancy, W. P., "A Limited Crystallographic and Optical Characterization of Alpha and Beta Silicon Nitride", Microscope, 22, 279-315 (1974).**

Characterization of micro crystals of Si_3N_4 formed by high pressure heat treatment of bulk Si_3N_4 in N. Extensive optical results were confirmed and complemented by electron microscopy and X-ray diffraction analysis. Found were α-Si_3N_4 pseudo-morphs of β-Si_3N_4 as well as apparent twins of each phase.

127. **Claussen, N., and Lahmann, C. P., "Fracture Behavior of Some Hot-Pressed Si_3N_4 Ceramics at High Temperature", Powder Met. Int., 7, 133-135 (1975).**

The temperature dependence of flexural strength and fracture toughness (K_{Ic}) of Si_3N_4 hot pressed with addition of MgO, Al_2O_3, and ZrO_2 was investigated. The Al containing material showed greater high-temperature strength, but lower fracture toughness than the material containing Mg. ZrO_2 additions increase toughness of the Al material, and ZrO_2 particles control crack propagation.

128. **Cockbain, A. G., "Strain in Hot Pressed Dense Silicon Nitride", Proc. Brit. Ceram. Soc., No. 25, 253-261 (1975).**

Circumferential displacements that occur when hot-pressed Si_3N_4 cylinders are sliced longitudinally indicated strain. Residual stresses affect reproducibility of mechanical properties and no treatment has been found for eliminating them.

129. **Collins, J. F., and Gerby, R. W., "New Refractory Uses for Silicon Nitride Reported", J. Metals, 7, 612-615 (1955).**

Techniques for fabrication of Si_3N_4 by pressing, slip-casting, and extrusion are discussed. All techniques yield articles approximately 72% of the theoretical density. Physical properties, electrical and thermal properties, chemical properties, oxidation resistance, and applications of Si_3N_4 are reviewed.

130. **Colquhoun, I., Thompson, D. P., Wilson, W. I., Grieveson, P., and Jack, K. H., "The Determination of Surface Silica and Its Effect on the Hot-Pressing Behavior of Alpha-Silicon Nitride Powder", Proc. Brit. Ceram. Soc., No. 22, 181-195 (1973).**

Chemical methods for determining the amorphous SiO_2 covering the particles in α-Si_3N_4 powders are given and the results compared with O analysis by neutron activation. Pseudo-isostatic hot pressing of Si_3N_4 is described. The effect of additives on the surface SiO_2 is explained; MgO and Al_2O_3 additives reduce its effects, C reacts with SiO_2 to produce CO which converts Si_3N_4 to SiC.

131. **Colquhoun, I., Wild, S., Grieveson, P., and Jack, K. H., "Thermodynamics of the Silicon-Nitrogen-Oxygen System", Proc. Brit. Ceram. Soc., No. 22, 207-227 (1973).**

Thermodynamic measurements for phases in the Si-N-O system were made at 50 C intervals in the range of 1200-1500 C and the limiting conditions for each phase formation are expressed in terms of N and O partial pressures. Experimental data are not sufficiently accurate to predict the exact temperature at which transformations will occur between the phases in the Si-N-O system. Data confirms that α-Si_3N_4 is an oxynitride with a limited range of homogeneity $Si_{11.4}N_{15}O_{0.3}$ - $Si_{11.5}N_{15}O_{0.5}$.

132. **Coppola, J. A., Bradt, R. C., Richerson, D. W., and Alliegro, R. A., "Fracture Energy of Silicon Nitrides", Bull. Amer. Ceram. Soc., 51, 847-851 (1972).**

Fracture surface energies of four hot-pressed and two reaction-sintered Si_3N_4 materials were measured from -196 to 1400 C by work of fracture technique. Fracture energy first decreased with increasing temperature and then, at higher temperature, increased rapidly. Hot-pressed materials had higher fracture surface energies than the reaction-sintered materials.

133. **Cutler, I. B., and Croft, W. J., "Powder Metallurgy Review 7: Silicon Nitride (Part 1)", Powder Met. Int., 6, 92-96 (1974); "(Part 2)", Powder Met. Int., 6, 144-146 (1974).**

Review of the properties of Si_3N_4 important to utilization at high temperatures such as crystal structure, density, thermodynamics, thermal expansion, and strength. Some of the areas needing more detailed investigation are pointed out.

Also published as Report AD 769 680, National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia. Report includes Appendix: "European Organizations Concerned with Si_3N_4 and Associated High Temperature Ceramics", includes the names of the principal investigators and the nature of their projects.

134. **Dalal, H. M., Chiu, Y. P., and Rabinowicz, E., "Evaluation of Hot Pressed Silicon Nitride as a Rolling Bearing Material", ASLE Trans., 18, 211-221 (1975).**

Si_3N_4 can be lubricated satisfactorily by conventional lubricants. Its abrasive wear coefficient is high compared to other ceramics. Rolling-contact fatigue and spalling behavior were compared to steel. Attempts were made to reduce severity of surface interactions between Si_3N_4 and M50 steel.

135. **Dalgleish, B. J., and Pratt, P. L., "The Influence of Microstructure on the Strength of Reaction-Bonded Silicon Nitride", Proc. Brit. Ceram. Soc., No. 25, 295-310 (1975).**

Fracture strengths to 1600 C were measured on reaction-sintered materials varying in pore size, α/β ratio, and density. γ_i values were determined by crack growth and double torsion techniques. Agreement between measured and calculated values suggests that largest pores control strength.

136. **Dalgleish, B. J., and Pratt, P. L., "The Microstructure of Reaction-Bonded Silicon Nitride", Proc. Brit. Ceram. Soc., No. 22, 323-326 (1973).**

Microstructure of reaction-bonded Si_3N_4 was studied during nitridation, using scanning and transmission electron, and optical microscopy. At temperatures below the melting point of Si the pores of the compact became filled with needles which form the background matte of α-Si_3N_4. At temperatures above the melting point there is increased growth of β-Si_3N_4 resulting in formation of a two-phase structure.

137. **Davidge, R. W., and Evans, A. G., "The Strength of Ceramics", Mater. Sci. Eng., 6, 281-298 (1970).**

Review of high-strength ceramics, oxides, nitrides, and carbides, with potential high-temperature applications. A unified materials science approach to strength which can be applied to promote a fundamental understanding of the strength of any ceramic material is presented. Three ranges of fracture behavior were identified: (Region A) fracture from inherent flaws, (Region B) fracture from flaws generated by small amounts of plastic deformation, (Region C) fracture after considerable plastic deformation. In case of Si_3N_4 temperature has very little effect on strength if plastic effects are absent.

138. **Davies, D.G.S., "The Statistical Approach to Engineering Design in Ceramics", Proc. Brit. Ceram. Soc., No. 22, 429-452 (1973).**

Results of strength studies on Si_3N_4 specimens are analyzed by Weibull function and the applicability of this function is assessed. A more general theory including Weibull theory as a special case is outlined.

139. **de Biasi, V., "2500 F Ceramics R&D Payoff", Gas Turbine World, 4, 12-15 (1974).**

Review of Westinghouse's ceramic R and D program for the design application of brittle materials for high-temperature stationary gas turbine operations.

140. **Deely, G. G., Herbert, J. M., and Moore, N. C., "Dense Silicon Nitride", Powder Met., No. 8, 145-151 (1961).**

Method of preparing Si_3N_4 bodies of almost theoretical density. Si_3N_4 powder is hot pressed with a small proportion of catalyst MgO or Mg_3N_2 at 1850 C. Physical properties of dense material indicate it should be suitable for use in making components required to operate under high stress at temperatures up to ~1200 C.

141. **Desmaison, J., Giraud, D., and Billy, M., "Recherches sur les nitures de silicium. III. Le chloroimidodisilane formé par action du chlorure d' ammonium sur l' imide $Si_2(NH)_3$", Rev. Chim. Miner., 9, 417-430 (1972).**

A chloroimidodisilane, $Si_8N_{10}H_{11}Cl_5$ is formed by the reaction of NH_4Cl with the imide $Si_2(NH)_3$. Its thermolysis leads to a silicon-chloronitride which is stable under vacuum up to 700 C. At high temperature the Cl is eliminated and an α-Si_3N_4 is formed.

142. **Dragomir, C., and Oprea, G., "Contributions to the Studies of Refractories of Silicon Nitride and Silicon Oxynitride", Cercet. Metal. Inst. Cercet. Metal., Bucharest, 16, 633-663 (1975). (In Romanian)**

N-O mixture was used instead of pure N to prepare Si_2ON_2 with very little contamination by Si_3N_4. The maximum oxynitridation was obtained at a Si-SiO_2 ratio of 6:1.

143. **Drew, P., and Lewis, M. H., "The Microstructure of Silicon Nitride/Alumina Ceramics", J. Mater. Sci., 9, 1833-1838 (1974).**

The microstructures of materials formed by sintering or hot pressing Si_3N_4 and Al_2O_3 were studied by transmission electron microscopy. It is proposed that β'-silicon aluminum oxynitride forms by a liquid phase mechanism analogous to that involved in the α/β Si_3N_4 phase transformation. The origin and crystallography of the "x-phase" is discussed.

144. **Drew, P., and Lewis, M. H., "The Microstructures of Silicon Nitride Ceramics During Hot-Pressing Transformations", J. Mater. Sci., 9, 261-269 (1974).**

The microstructure of fine grained ($<1\mu m$) Si_3N_4 with an MgO additive was studied by electron microscopy at various stages in the hot-pressing process: 1) initial Si_3N_4 (~90%α) powder, 2) partially densified and partially transformed α- to β-Si_3N_4, 3) almost fully dense and fully transformed β-Si_3N_4. A solid/liquid/ solid transformation mechanism is suggested.

145. **Eckerlin, V. P., "Die Kristallstruktur von $BeSiN_2$", A. Anorg. Chem., 353, 225-236 (1967).**

Structure was determined on crystals obtained by sublimation. Space group is Pn a 2_1 with unit cell parameters a = 4.977, b = 5.747, c = 4.674Å; Z = 4. This ABX_2 structure is an analogue to the superstructure of sphalerite known as chalcopyrite.

146. **Edington, J. W., Rowcliffe, D. J., and Henshall, J. L., "Powder Metallurgical Review 8: The Mechanical Properties of Silicon Nitride and Silicon Carbide. Part I: Materials and Strength", Powder Met. Int., 7, 82-96 (1975).**

Reviews the mechanical properties of commercially available Si_3N_4 and SiC and some of the more promising experimental materials. The importance of crack initiation and propagation in emphasized. The fracture mechanics and Weibull statistical approaches are summarized. Outlined are essential features of materials, manufacturing methods, microstructure, and crystal structure, followed by treatments of elastic constants and strength. Included are 171 references.

147. **Edington, J. W., Rowcliffe, D. J., and Henshall, J. L., "Powder Metallurgical Review 8: The Mechanical Properties of Silicon Nitride and Silicon Carbide. Part II: Engineering Properties", Powder Met. Int., 7, 136-147 (1975).**

Engineering properties of Si_3N_4 and SiC such as fracture toughness, creep and fatigue together with the possibilities of failure prediction and future materials improvement are summarized. Included are 106 additional references.

148. **Edwards, A. J., Elias, D. P., Lindley, M. W., Atkinson, A., and Moulson, A. J., "Oxygen Content of Reaction-Bonded α-Silicon Nitride", J. Mater. Sci., 9, 516-517 (1974).**

Oxygen contents were determined on reaction-sintered Si_3N_4 by neutron activation analysis. Results indicate that little or no O is required for α-Si_3N_4 to be stable.

149. **Elias, D. P., and Lindley, M. W., "Reaction Sintered Silicon Nitride. Part I: The Influence of Oxygen and Water Vapour Contamination on Strength and Composition", J. Mater. Sci., 11, 1278-1287 (1976).**

Chemical contamination of nitriding gas by O and H_2O to high concentrations does not degrade strength. Coefficient of variation in strength and "apparent" crystallite size are related to H_2O concentration in gas. Also considers formation of α- and β-Si_3N_4 and suggests that α-composition is fixed.

150. **Engel, W., Porz, F., and Thuemmler, F., Ber Dtsch. Keram. Ges., 52, 296-299 (1975). (See Entry No. 436)**

151. **Engel, W., and Thuemmler, F., "Kreichverhalten von reaktionsgesintertem Si_3N_4 bei 1200 bis 1400 C", Ber. Deut. Keram. Ges., 50, 204-210 (1973).**

Creep behavior in four-point bend in air at loads to 60 MN/m^2 of reaction-sintered Si_3N_4 (density 2.05-2.33 g/cc) was investigated. Mechanisms considered include dislocation motion and grain boundary sliding.

152. **Evans, A. G., and Davidge, R. W., "The Strength and Oxidation of Reaction-Sintered Silicon Nitride", J. Mater. Sci., 5, 314-325 (1970).**

Scanning electron and optical microscopy were used to study the structure of reaction-sintered Si_3N_4 at various stages during nitriding for a range of nitriding and compacting conditions. Strength was evaluated and interpreted in terms of microstructure. Fracture always occurred in a brittle manner by extension of the largest pores. Effects of prolonged annealing in air above 1000 C on structure and strength were investigated. Cristobalite was formed at 1400 C. Strength was enhanced if temperature was then maintained above 250 C. Below this temperature cracks in the oxide layer lessen the strength.

153. **Evans, A. G., Russell, L. R., and Richerson, D. W., "Slow Crack Growth in Ceramic Materials at Elevated Temperatures", Met. Trans. A., 6A, 707-716 (1975).**

Data suggests that slow crack growth of a range of Si_3N_4 materials between 1100-1400 C may be characterized by the relation between crack velocity and stress intensity factor. Data indicate that fatigue behavior can be predicted with moderate accuracy from isothermal, static stress parameters. The application of slow crack growth data to failure predictions is described and illustrated.

154. **Evans, A. G., and Sharp, J. V., "Microstructural Studies on Silicon Nitride", J. Mater. Sci., 6 (10), 1292-1302 (1971).**

Thin specimens of reaction-sintered and hot-pressed Si_3N_4 have been prepared by ion beam thinning and examined in the Harwell million-volt microscope. The reaction-sintered material consists of large grains, mostly β-Si_3N_4, in a fine-grained matrix of α-Si_3N_4. The types of fibers observed within the pores depend on the size of the pore. The hot-pressed material consists largely of small angular grains of β-Si_3N_4 and large irregular grains. The grains of β-Si_3N_4 generally contain dislocations having a <0001> Burgers vector.

155. **Evans, A. G., and Wiederhorn, S. M., "Crack Propagation and Failure Prediction in Silicon Nitride at Elevated Temperatures", J. Mater. Sci., 9, 270-278 (1974).**

Technique for studying high-temperature crack propagation in ceramics was developed and applied to study crack propagation rate and stress intensity factor for hot-pressed Si_3N_4 to 1400 C. Data are used to develop proof testing criteria.

156. **Evans, J. W., and Chatterji, S. K., "Kinetics of the Oxidation and Nitridation of Silicon at High Temperatures", J. Phys. Chem., 62, 1064-1067 (1958).**

Kinetic behavior of Si in O, CO_2, N, and Ar-0.2%N was determined at 1200-1400 C by means of a thermo-balance. In O and CO_2 the rate laws were shown to be parabolic. In pure N erratic behavior was observed with the formation of volatile Si_3N_4. At a low pressure of N in Ar volatilization was absent and a logarithmic rate law was shown to hold.

157. **Fate, W. A., "Density Dependence of Shear Modulus of Si_3N_4", J. Amer. Ceram. Soc., 57, 372 (1974).**

Room-temperature shear modulus was measured for seven Si_3N_4 samples in the density range 2.37-3.18 g/cm^3 using the pulsed ultrasonic method. Shear modulus increased smoothly with sample density.

158. **Fate, W. A., "High Temperature Elastic Moduli of Polycrystalline Silicon Nitride", J. Appl. Phys., 46, 2375-2377 (1975).**

Elastic modulus data are given for some commercially available Si_3N_4 having densities between 2.37 and 3.18 g/cm^3 at temperatures from 0 to 1000 C. The density dependence of elastic constants is in approximate agreement with a theory of composite materials.

159. **Fate, W. A., "High-Temperature Shear Modulus of Si_3N_4 and SiC", J. Amer. Ceram. Soc., 57, 49-50 (1974).**

Shear moduli were obtained for hot-pressed Si_3N_4 and SiC specimens in the range 350-1000 C using a pulse-echo technique. For Si_3N_4 the shear modulus is a smoothly decreasing function of temperature in this range. Room temperature results were ~5% hower than those at 350 C.

160. **Feld, H., Ettmayer, P., and Petzenhauser, I., "Sauerstoffstabilisierung von α-Si_3N_4", Ber. Deut. Keram. Ges., 51, 127-131 (1974).**

Si_3N_4 consisting of ~85% α-Si_3N_4 and 1.95-2.85% O was prepared and annealed 2, 4, 8, and 16 hours at 1600 C converting the α-phase to β-phase which contained no O. During the process the O content decreased as N content increased. Suggest α-Si_3N_4 has composition $Si_{23}N_{30}O$.

161. **Felten, R. P., "Siliziumnitrid - eine Literaturübersichte", Sprechsaal Keram. Glas. Baustoffe, 3, 92-96, 101-110 (1974).**

A literature survey covering the structure, preparation, properties, and reactions of Si_3N_4 with 51 references.

162. **Fickel, A., "Herstellung und Anwendungsmöglichkeiten von Siliziumnitrid-Werkstoffen", VC-Chem. Tech., 2, 155-159 (1973).**

Review of processing, properties, and applications of reaction-sintered and hot-pressed Si_3N_4.

163. **Fickel, A. F., "Neue keramische Werkstoff", Chem-Tech. (Heidelberg), 4, 317-320 (1975).**

Review of preparation and properties of reaction-sintered and hot-pressed Si_3N_4.

164. **Fickel, A. F., and Kessel, H., "Technologie und Anwendung von dichtem Siliziumnitrid", Glas. Email. Keram. Tech., 25, 193-196 (1974).**

Production of hot-pressed and reaction-bonded Si_3N_4 is described. In order to study the production parameters, an induction-heated vacuum hot press was constructed, allowing production of pieces up to 300 mm diam. Possible applications as a corrosion- and abrasion resistant material with great strength even at high temperatures are discussed.

165. **Finkel'shtein, I. N., "Silicon Nitride Based Structural Ceramics", Teknol. Organ. Protzvod., 1, 62-64 (1974). (In Russian)**

Discusses refractories made from various Si_3N_4-Cr_2O_3 compositions.

166. **Finkel'shtein, I. N., "Some Properties of Materials of the System Si_3N_4-ZrO_2", Sov. Powder Met. Metal Ceramics, 13, 512-514 (1974).**

Examined porosity, refractoriness, thermal stability, impact strength, compressive strength, and thermocycling effect on the mechanical properties of hot-cast Si_3N_4-ZrO_2 ceramic samples containing 20, 40, 60, 80, 100% of Si_3N_4.

167. **Forgeng, W. D., and Decker, B. F., "Nitrides of Silicon", Trans. AIME, 212, 343-348 (1958).**

X-ray data are given for the two modifications of Si_3N_4, an oxynitride of silicon, Si_2ON, and a material prepared by the fusion of commercial Si_3N_4. The pattern for pure α-Si_3N_4 is less complex than previously reported and has been indexed on a hexagonal rather than orthorhombic cell. β-Si_3N_4 and the fused material (Si_xN) have hexagonal structures which appear to be related to that of α-Si_3N_4. The pattern of the oxynitride, although complex, can be indexed as orthorhobmic.

168. **Funke, V. F., and Samsonov, G. V., "Preparation and Certain Properties of Silicon Nitride", Zh. Obsch. Khim., 28, 267-272 (1958). (In Russian)**

Two methods of preparation were studied. In the first, a SiO_2-C mixture (molar ratio 1:2) was heated in a current of N at 1400-1800 C to yield Si_3N_4 and SiC in 2-4% and 15-85% respectively. In the second, Si powder was heated in N (at 1 atm) at 970-1600 C for times up to 25 hours, the Si_3N_4 content being determined by X-ray diffraction. Data are tabulated and plotted. The Si_3N_4 phase has no region of homogeneity.

169. **Galasso, F., Kuntz, U., and Croft, W. J., "Pyrolytic Si_3N_4", J. Amer. Ceram. Soc., 55, 431 (1972).**

Thick films of α-Si_3N_4 were prepared by reacting SiF_4 and NH_3 on hot carbon substrates at 1100-1550 C and pressure of 1 to 10 mm of Hg. The deposition rate varied from 1×10^{-4} to 1×10^{-2} in/hr over the temperature range. Corrosion, electrical and thermal property data are given for the pyrolytic material thus obtained.

170. **Gauckler, L. J., Lukas, H. L., and Petzow, G., "Contribution to the Phase Diagram Si_3N_4-AlN-Al_2O_3-SiO_2", J. Amer. Ceram. Soc., 58, 346-347 (1975).**

Presentation and discussion of isothermal section at 1760 C.

171. **Gauckler, L. J., Lukas, H. L., and Tien, T. Y., "Crystal Chemistry of β-Si_3N_4 Solid Solutions Containing Metal Oxides", Mater. Res. Bull., 11, 503-512 (1976).**

A review of phase diagrams of Si_3N_4-metal oxides systems showed that the solid solubility limits of the metal oxides depends on the size and charge of the metal elements. A misfit factor is defined which can specify these limits. When the misfit factor is small, a substantial amount of foreign atoms can be accommodated in the β-Si_3N_4 lattice, but as it becomes larger, only a small amount of foreign atoms enter the lattice.

172. **Gazza, G. E., "Effect of Yttria Additions on Hot-Pressed Si_3N_4", Bull. Amer. Ceram. Soc., 54, 778-781 (1975).**

Various grades of Si_3N_4 powder were hot pressed with additions of Y_2O_3 to 20 w/o. The effects of powder purity, percent addition, and testing temperature on resultant properties are discussed with supplemental evidence from crystallographic and Auger analyses.

173. **Gazza, G. E., "Hot-Pressed Si_3N_4", J. Amer. Ceram. Soc., 56, 662 (1973).**

Additions of 1.0-3.3 w/o Y_2O_3 to a high α-phase Si_3N_4 powder hot pressed in graphite dies in a N atmosphere at 6000-7000 psi produced fully dense compacts (3.22-3.26 g/cm^3 increasing with the amount of additive used) at 1750 C. Modulus of rupture at room temperature and at 1315 C was 118,000 psi 58,000-69,000 psi respectively.

174. **Gebhardt, J. J., Tanzilli, R. A., and Harris, T. A., J. Electrochem. Soc., 123, 1578-1582 (1976). (See Entry No. 26)**

175. **George, W., "Thermal Property Measurements on Silicon Nitride and Silicon Carbide Ceramics Between 290 and 700 K", Proc. Brit. Ceram. Soc., No. 22, 147-167 (1973).**

Thermal diffusivity, thermal conductivity, and specific heat measurements for a range of Si_3N_4 ceramics with densities between 1990 and 3070 kg m^{-3} are presented. Conductivities vary between 7 and 36 W m^{-1} K^{-1} at 302 K, possibly due to the varying amounts of "free silicon" phase in them. In the SiC ceramics examined the "free silicon" phase reduced the thermal conductivity. Thermal diffusivity values for SiC are also presented.

176. **Gill, R. M., and Spence, G., "Self-Bonded Silicon Nitride", Refract. J., 38 (3), 92-94, 96 (1962).**

Self-bonded Si_3N_4 is commercially manufactured and can be readily used to produce accurate components and has refractory and chemical properties which make it an attractive material for special refractory applications. Some are listed, but it is expected that the uses for this material will be ever-increasing.

177. **Glemser, O., Beltz, K., and Naumann, P., "The Silicon Nitrogen System", Z. anorg. u. allgem.Chem., 291, 51-66 (1957). (In German)**

Si_3N_4 was prepared by passing N or NH_3 over Si at 1230-1450 C or 1350 C respectively or by heating $Si(NH)_2$ at 1350 C. Powder diffraction studies showed $Si(NH)_2$ decomposition produced pure α-Si_3N_4. The Si-NH_3 reaction gave chiefly α- and a little β-Si_3N_4 and the Si-N reaction gave α-β mixture in which the α-form was favored at low temperatures. Electron microscopic studies are reported.

178. **Glenny, E., and Taylor, T. A., "Mechanical Strength and Thermal Fatigue Characteristics of Silicon Nitride", Powder Met., No. 8, 164-195 (1961).**

Mechanical properties, thermal shock and thermal fatigue characteristics of three reaction-sintered (density 1.9-2.6 g/ml) and one hot-pressed (density 3.0-3.18 g/ml) samples of Si_3N_4 differed according to composition and method of manufacture. Resistance to creep at 1000-1200 C and to thermal fatigue at 1000 C, particularly of the dense grades, can be considerably superior to that of creep-resistant alloys. The appreciable variation in performance of all grades indicates further development of the manufacturing technique is necessary.

179. **Gnesin, G. G., and Osipova, I. I., "Wesr-Resistant Engineering Materials Based on Silicon Nitride", Russ. Eng. J., 54 (12), 33-36 (1974). Translation of Vestnik Mashinostr. No. 12, 32-34 (1974).**

Discussion of possible applications of Si_3N_4 in turbine blades, bearings, piston rings, cutting tools, and electronic apparatus.

180. **Godfrey, D. J., "Ceramics for High-Temperature Engineering?", Proc. Brit. Ceram. Soc., No. 22, 1-25 (1973).**

Ceramics are being considered for use in high-temperature engineering, especially gas-turbine components. Unlike superalloys, ceramics offer 400-600 C increases in component temperatures without blade cooling. Glass-ceramics may be used up to ~1100 C above this temperature and up to 1400 C Si_3N_4 and SiC may be used. Properties and processing techniques for fully dense and incompletely dense Si_3N_4 and SiC are described. Design problems are examined and solutions suggested. Advantages of using ceramics are outlined and examples of a few successful applications are given.

181. **Godfrey, D. J., "The Effects of Impurities, Additions and Surface Preparation on the Strength of Silicon Nitride", Proc. Brit. Ceram. Soc., No. 25, 325-337 (1975).**

The effect of impurities containing Fe and Al in the formation of Si_3N_4 from pure Si powders was investigated. Additions of SiC or Al_2O_3 reduced strengths in proportion to the amounts added; the β-Si_3N_4 content increased in proportion to the Al_2O_3 added. Surface grinding of reaction-bonded Si_3N_4 either reduced or did not affect its strength in the as-fired condition, but reduced the strength degradation and oxidation resulting from 250 hours exposure in air at 1250 C.

182. **Godfrey, D. J., "The Fabrication and Properties of Silicon Nitride Ceramics and Their Relevance to Aerospace Applications", J. Brit. Interplanet. Soc., 22, 353-368 (1969).**

The absence of dimensional change during the nitridation consolidation of Si powder compacts during the fabrication of reaction-bonded Si_3N_4 is discussed. This facilitates the production of large, precision or joined ceramic shapes. Pressing, flame-spraying, and plastic-binder dough techniques for compaction of Si_3N_4 are described. A new and promising method of reinforcing Si_3N_4 matrices with high strength fibres is explained. A critical review of the preparation of Si_3N_4 relevant to aerospace applications is made. Also published as Report N69-34160, National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia.

183. **Godfrey, D. J., "The Use of Ceramics in High Temperature Engineering", Metals Mater., 2 (10), 305-311 (1968).**

High-temperature ceramics and their properties are compared to metals and alloys and their properties. Properties and use of these ceramics, including Si_3N_4, are reviewed.

184. **Godfrey, D. J., and Lindley, M. W., "The Strength of Reaction-Bonded Silicon Nitride Ceramics", Proc. Brit. Ceram. Soc., No. 22, 229-252 (1973).**

Strength data for flame-sprayed and isostatically-pressed Si_3N_4 materials are given. The effects of void content and surface finish on strength are discussed and results of the influence of surface addition of SiO and H_2O vapor in the nitriding atmosphere are presented. A comparison is made of strength data obtained for 3-point and 4-point bend specimens with two different spans.

185. **Godfrey, D. J., and Mitchell, K. W., "Statistical and Practical Approaches to the Development of Design Criteria for Brittle Materials", Materials for Engineers Series, edited by N. L. Parr,The Engineer, 224, 737-738 (1967).**

The development of composite materials, as fiber reinforced ceramics, having appreciable fracture toughness could be a way of obtaining meaningful improvements in the robustness of brittle material components. Only by sustained experimentation, as described, will any useful progress be made in the future.

186. **Godfrey, D. J., and Taylor, P. G., "Designing with Brittle Materials", Eng. Mater. Design, 12 (9), 1339-1342 (1969).**

Experiences in the use of a brittle ceramic material in engineering applications have given some hope that a means of employing such strong materials despite their brittleness will be found by designers. The ready fabricability of Si_3N_4 has provided a valuable tool in the development of a design philosophy for the use of brittle materials in high temperature engineering but many years of study will be required before a useful measure of success is obtained.

187. **Gostelow, C. R., and Restall, J. E., "Ceramics with Potential for Gas-Turbine Application", Proc. Brit. Ceram. Soc., No. 22, 117-127 (1973).**

Hot-pressed Si_3N_4 and reaction-bonded SiC, the ceramics with the most potential for application in gas turbine engines, have some limitations, but the possible areas and temperature regions where they may be used are discussed. Laboratory data on the effect of oxidation exposure at temperatures up to 1400 C are presented. Also discussed are glass-ceramics, one of which is useful to 1100 C.

188. **Goursat, P., Giraud, D., and Billy, M., "Étude du système silicium-oxygène-azote. III. - Le triimidodisiloxane $Si_2O(NH)_3$", Bull. Soc. Chem. Fr., No. 10, 3681-3683 (1972).**

Thermal decomposition of title compound yields Si_2ON_2.

189. **Goursat, P., Lotholary, P., and Billy, M., "Silicon-Oxygen-Nitrogen System: I, Preparation of the Oxynitride Si_2N_2O", Rev. Int. Hautes Temp. Refract., 8, 149-154 (1971). (In French)**

The oxynitride is formed by the reaction of $3Si + SiO_2 + 2N_2 \rightarrow 2Si_2N_2O$ above ≈1420 C in the presence of liquid Si.

190. **Grathwahl, G., and Thuemmler, F., "Kriechen von Si_3N_4 unter oxidierenden und Bedingungen", Ber. Dtsch. Keram. Ges., 52, 268-270 (1975).**

Creep of reaction-bonded Si_3N_4 (2.11-2.40 g/cm^3) at 1200-1400 C is affected by the environment. Due to internal oxidation, creep in air is more severe than in vacuo. This is not true of hot-pressed Si_3N_4. Measures to prevent the internal oxidation are proposed.

191. **Gribkov, V. N., Silaev, V. A., Shchetanov, B. V., Umantsev, E. L., and Isaikin, A. S., "Growth Mechanism of Silicon Nitride Whiskers", Soviet Physics-Crystallography, 16 (5), 852-854 (1972). Translation of Kristallografiya, 16 (5), 982-985 (1971).**

Conditions and mechanisms for growth of α-Si_3N_4 whicker crystals from a (SiO_2 + Si) mixture in a N atmosphere, with the addition of H were investigated. The presence of mullite or Al, or Fe impurities in the Si is a necessary condition for growth. The condensation of Si_3N_4 from the gas phase proceeds by a VLS mechanism. The crystallization of α-Si_3N_4 from drops and the growth of the whiskers proceed according to an axial helical dislocation mechanism.

192. **Gruver, R. M., and Kirchner, H. P., "Effect of Leached Layers on Impact Damage and Remaining Strength of Silicon Nitride", J. Amer. Ceram. Soc., 59, 85-86 (1976).**

The formation of energy-absorbing layers by leaching hot-pressed Si_3N_4 and the effect of these layers on the formation of Hertzian cracks and the remaining strength are described.

193. **Gugel, E., Fickel, A. F., and Kessel, H., "Developments in the Production of Hot-Pressed Silicon Nitride", Powder Met. Int., 6, 136-140 (1974).**

History and present state-of-the-art of German research and development in the production of hot-pressed Si_3N_4 is described especially in relation to gas turbine applications. A device for producing Si_3N_4 pieces up to 30 mm diam is described. Properties and possible applications are discussed.

194. **Gugel, E., and Leimer, G., "Keramik en der Gasturbine", Ber. Deut. Keram. Ges., 50 (5), 151-155 (1973).**

Discussion of the use of ceramics, particularly Si_3N_4 and SiC, for achieving economical gas turbine operation through higher operating temperatures.

195. **Gugel, E., Petzenhauser, I., and Fickel, A., "X-ray Investigation of the System Si_3N_4-Al_2O_3 (On the Question of a 'Second' Phase in the System Al-Si-O-N)", Powder Met. Int., 7, 66-67 (1975).**

Solid solution in system reaches limit at $Si_{6-x}\ Al_x\ N_{8-x}\ O_x$. Authors propose second phase with composition $SiAlNO_2$.

196. **Gulden, M. E., and Metcalfe, A. G., "Stress Corrosion of Silicon Nitride", J. Amer. Ceram. Soc., 59, 391-396 (1976).**

Variable-strain rate and static fatigue tests performed on hot-pressed and reaction-sintered Si_3N_4 indicated time-dependent failure in an atmosphere of H_2O-saturated flowing air. The effect is moisture-dependent. A model for the mechanism of stress corrosion of hot-pressed Si_3N_4 is proposed.

197. **Guseva, E. A., Turchanin, A. G., Bolgar, A. S., Osipova, I. I., and Goncharuk, A. B., "High-Temperature Enthalpy of Silicon Nitride Base Materials", Sov. Powder Met. Metal Ceram., 13, 55-58 (1974). Translation of Porosh. Met., No. 1, 71-76 (1974).**

The enthalpy of four Si_3N_4-base materials 1) +5MgO, 2) +10MgO, 3) +5MgO + 20BN, 4) +10MgO + 20BN was measured, by the method of mixing, in a high-temperature calorimetric apparatus. Equations describing the temperature dependence and heat capacity were obtained by the least-square method.

198. **Guthrie, R. B., and Riley, F. L., "Effect of Oxide Impurities on the Nitridation of High Purity Silicon", J. Mater. Sci., 9, 1363-1365 (1974).**

Nitridation of Si powder in high-purity Al_2O_3 tubes was shown to enhance the formation of α-Si_3N_4. Suggest that the formation of β-Si_3N_4 is related to volatilization of impurities from muffle tubes.

199. **Guthrie, R. B., and Riley, F. L., "The Nitridation of Single-Crystal Silicon", Proc. Brit. Ceram. Soc., No. 22, 275-280 (1973).**

Thick films of predominantly α-Si_3N_4 having a tendency to be oriented with the (001) basal plane parallel to the (111) Si surface were formed when single-crystal semiconductor grade Si was heated in a controlled purity N atmosphere. Addition of low concentrations of O or H_2O into the N atmosphere leads to an increase in proportion of β-Si_3N_4 formed.

200. **Guzman, I. Ya., Litvin, Yu. N., and Turchina, G. V., "Oxidation Kinetics of Ceramics from Silicon Nitride and Oxynitride", Refractories, 15, 118-122(1974). Translation of Ogneupory, No. 2, 47-52 (1974).**

Kinetics of oxidation of porous β-Si_3N_4 and Si_2ON_2 were investigated from 900-1500 C by TG, dilatometry, and X-ray analysis. Effect of pore structure on oxidation is discussed.

201. **Guzman, I. Ya., Tumakova, Ye. I., and Fedotov, A. V., "Comparative Study of Some Properties of Materials Based on the Composition SiC-Si_3N_4 and SiC-Si_2ON_2", Refractories, 13, 667-670 (1973). Translation of Ogneupory, No. 10, 44-48 (1972).**

Compares properties of mixed materials with those of relatively pure Si_3N_4 and Si_2ON_2. The former materials are cheaper and useable under favorable service conditions.

202. **Hardie, D., and Jack, K. H., "Crystal Structure of Silicon Nitride", Nature, 180, 332-333 (1957).**

The two forms of Si_3N_4 were studied by X-ray powder diffraction photographs taken with Fe Kα radiation. α-Si_3N_4 is hexagonal with a unit cell containing 12 Si and 16 N atoms and is assigned to space group P 31c. β-Si_3N_4 is hexagonal with a unit cell containing 6 Si and 8 N atoms and is assigned to space group P63/m.

203. **Harrison, D. E., "Properties Important to the Design of Ceramic Stator Vanes for Industrial Gas Turbines", Proc. Brit. Ceram. Soc., No. 22, 391-408 (1973).**

Discusses design and fabrication of Si_3N_4 stator vanes. Stress analysis ignores time-dependent properties such as creep, fatigue, and corrosion-erosion but progress on the measurement of these properties is reviewed. Weibull statistics are used to relate tensile and bend strengths and high temperature (>1000 C) mechanical properties attributed to grain-boundary phases.

204. **Hartline, S. D., Bradt, R. C., Richerson, D. W., and Torti, M. L., "Work-of-Fracture and Apparent Yield Correlation in Si_3N_4", J. Amer. Ceram. Soc., 57, 190-191 (1974).**

The work-of-fracture and yielding behavior of two grades on hot-pressed Si_3N_4 are compared in the temperature range 1000-1400 C. The correlation of strength, σ_y/σ_f ratio, and work of fracture supports the idea that the intergranular bond controls the high temperature strength behavior of hot-pressed Si_3N_4.

205. **Hasselman, D.P.H., Chen, E. P., Ammann, C. L., Doherty, J. E., and Nessler, C. G., "Failure Prediction of the Thermal Fatigue of Silicon Nitride", J. Amer. Ceram. Soc., 58, 513-516 (1975).**

Slow crack-growth data were used to predict thermal fatigue life of Si_3N_4 parts in a turbine engine. Computer-predicted and experimental life were in agreement. Results suggest that minimizing grain-boundary phase will increase thermal fatigue resistance.

206. **Henderson, C.M.B., and Taylor, D., "Thermal Expansion of Nitrides and Oxynitride of Silicon in Relation to Their Structure", Trans. J. Brit. Ceram. Soc., 74, 49-53 (1975).**

Presents thermal expansion data up to 1020 C obtained by X-ray diffraction methods for α- and β-Si_3N_4 and Si_2ON_2 and discusses results in relation to crystal structures. It is suggested that α- and β-Si_3N_4 are moderately- and slightly-strained crystal structures, respectively, and that this hypothesis may explain much of their behavior.

207. **Hincke, W. B., and Brantley, L. R., "The High Temperature Equilibrium Between Silicon Nitride, Silicon, and Nitrogen", J. Amer. Chem. Soc., 52, 48-52 (1930).**

The pressure of N at which equilibrium prevails between Si_3N_4 and its elements at absolute temperatures ranging from 1606 to 1802 K was determined. This pressure is 0.27 mm at 1606 K and 5.5 mm at 1802 K. Within this temperature interval the free energy increase at one atmosphere for the reaction $Si_3N_4 = 3Si + 2N_2$ can be expressed as $\Delta F = 176{,}300 - 78.35T$ calories. It can be concluded that the dissociation pressure of the nitride becomes one atmosphere at about 2250 K.

208. **Hofmann, S., and Gauckler, L. J., "A Study of Fracture Surfaces of Hot-Pressed Silicon Nitride by Auger Electron Spectroscopy", Powder Met. Int., 6, 90-92 (1974).**

Auger spectra are given for fracture surfaces of hot-pressed Si_3N_4 containing 5w/oMgO and of "sialon" containing 43w/oAl_2O_3. Results on the former material suggest an O rich grain-boundary phase (containing Si, Ca, and Mg) 20-30Å thick.

209. **Hofmann, S., Gauckler, L. J., and Tillmann, L., "Auger Electron Microscopy on the Fracture of Nickel-Tungsten Materials and Silicon Nitride", Mikrochim. Acta, Suppl., 6, 373-382 (1975). (In German)**

O accumulation on grain boundaries in Si_3N_4 was attributed to addition of MgO or Al_2O_3.

210. **Horton, R. M., "Oxidation Kinetics of Powdered Silicon Nitride", J. Amer. Ceram. Soc., 52 (3), 121-124 (1969).**

Oxidation kinetics of powdered Si_3N_4 were studied in dry O and dry air at 1 atm pressure between 1065 and 1340 C. An automatic recording electrobalance was used to measure the weight gain as a function of time. Parabolic oxidation kinetics were observed with activation energies of 61 kcal/mol in dry O and 68 kcal/mol in dry air. The oxidation rate in dry O was approximately twice that in air. The solid oxidation product was tridymite above 1125 C and amorphous silica at 1067 C.

211. **Huebner, K., "Silicon Nitride, a Ceramic Material With Outstanding Temperature-, Shock-, and Corrosion-Resistance", Chem. -Ztg., 95 (22), 931-934 (1971). (In German)**

The crystal structure and physical, mechanical, and chemical properties of sintered Si_3N_4, and its use in crucibles, pipes, nozzles, and tiles are reviewed with 16 references.

212. **Huseby, I. C., Lukas, H. L., and Petzow, G., "Phase Equilibria in the System Si_3N_4-SiO_2-BeO-Be_3N_2", J. Amer. Ceram. Soc., 58, 377-380 (1976).**

The 1780 C isothermal section of the system was investigated by X-ray analysis of hot-pressed samples. The equilibrium relationships shown involve previously known compounds and eight newly found compounds.

213. **Huseby, I. C., and Petzow, G., "Influence of Various Densifying Additives on Hot-Pressed Si_3N_4", Powder Met. Int., 6, 17-19 (1974).**

Hot-pressing of Si_3N_4 powders containing various additives was characterized by X-ray diffraction and hot hardness measurements. Useful densification aids include BeO, CeO_2, Ce_2O_3, and La_2O_3 at the 4.5v/o level. Texture of resulting β-Si_3N_4 compacts is discussed.

214. **Hüttinger, K. J., "The Effect of Oxygen Traces on the Nitriding of High-Purity Silicon Between 1250 and 1380 C", High Temp.-High Pressures, 2, 89-93 (1970).**

Semiconductor-grade single-crystal Si disks cut parallel to the (111) plane were reacted with N, previously freed from 0, at 1250-1380 C and their weight changes recorded. The reaction layers were analyzed by electron microprobe and X-ray techniques, and examined by light and scanning electron microscopy. Even trace quantities of O were found to have a decisive effect on the reaction.

215. **Hüttinger, K. J., "The Kinetics of the Nitriding of Silicon", High Temp.-High Pressures, 1, 221-230 (1969). (In German)**

The kinetics of the reaction of Si(>99% pure) with N were studied thermogravimetrically. Contrary to the results of earlier investigations, a linear dependence was established for the growth of the Si_3N_4 layer, both above and below the melting point of Si. The activation energy for the gas/solid reaction was found to be 156 kcal $mole^{-1}$. The purity of Si has an appreciable effect on the reaction kinetics. Traces of O have a strong inhibiting effect on the reaction as well as favoring the formation of α-Si_3N_4.

216. **Hyde, C., "Silicon Nitride Finds Application as Roller-Bearing Material", Engineer, 283, 45 (30 May 1974).**

Commercial hot-pressed Si_3N_4 has fatigue properties 8 times better than those of M50 CVM steel at a stress of 4175 MN/m^2. Desirable properties include good corrosion resistance and low coefficients of expansion and friction.

217. **Ichinose, A., and Einaga, H., "Determination of Nitrogen and Silicon in Silicon Nitride", Yogyo Kyokai Shi, 83, 465-470 (1975).**

N content of Si_3N_4 was determined by decomposition in NaOH at ~320 C and collecting NH_3 in a boric acid solution with the aid of steam vapor as a carrier. Solution is titrated with a standard acid solution against methyl red. A conventional gravimetric method was used to determine Si.

218. **Idrestedt, I., and Brosset, C., "Structure of Si_2N_2O", Acta Chem. Scand., 18, 1879-1886 (1964).**

Crystal structure of Si_2N_2O was determined by X-ray crystallographic methods. The crystals are orthorhombic, the space group $Cmc2_1$ and the unit cell dimensions are: a = 8.843 ± 0.005 Å, b = 5.473 ± 0.005 Å, c = 4.835 ± 0.005 Å, and there are four formula units in the cell.

219. **Inomata, Y., "Nitridation of Silicon Powder", Yogyo Kyokai Shi, 83, 497-500 (1975).**

Products of the reaction between Si powder and N were observed by electron microscopy to establish the morphological features relating to the kinetics. The proportionality of the reaction rate to the square root of the particle diameter was consistent with Griffiths theory. Activation energy of 156-158 kcal/mol was ascribed to N diffusion through Si_3N_4 layer.

220. **Inomata, Y., "Oxidation Resistant Si-Impregnated Surface Layer of Reaction Sintered Nitride Articles", Yogyo Kyokai Shi, 83, 1-3 (1975).**

Stable Si layers 40-100 μm thick were formed on reaction-sintered Si_3N_4 by heating 10-15 minutes at 1430-1450 C in N. Layers were protected against oxidation to 1400 C. Effect of O pressure on wetting is briefly discussed.

221. **Inomata, Y., "Stability Relation in the System β-Silicon Nitride - α-Silicon Nitride - Silicon Oxynitride (Si_2N_2O) and Their Structural Change by Heating Above 1600°", Yogyo Kyokai Shi, 82, 522-526 (1974). (In Japanese)**

Experiments were performed on heating Si_3N_4 and Si_2N_2O samples at 1530-1730 C under 1 atm of N and the change of composition studied by X-ray diffrection. Results showed that the stable compound in the system Si-N_2 (1 atm)-O_2 changes in the order β-$Si_3N_4 \rightarrow Si_2N_2O \rightarrow SiO_2$ according to the increasing partial pressure of O and that α-Si_3N_4 is unstable under the same conditions. SiO (g) has an important role in the oxidation of Si_3N_4 and Si_2N_2O at elevated temperatures.

222. **Inomata, Y., "Thermal Stability of α-Silicon Nitride in the System Silicon-Nitrogen-Oxygen at 1730°", Yogyo Kyokai Shi, 82, 508 (1974). (In Japanese)**

A pellet comprising an equimolecular mixture of Si_3N_4 and amorphous SiO_2 powders was embedded in the same SiO_2 powders and heated for 8 hours at 1730 C in N. The stable compounds observed were β-Si_3N_4-Si_2N_2O, and SiO_2 but not α-Si_3N_4.

223. **Inomata, Y., and Inoue, Z., "Decomposition Temperature of Silicon Nitride in the System Si_3N_4-C-N_2 (1 atm)", Yogyo Kyokai Shi, 81, 441-444 (1973).**

The decomposition temperature of Si_3N_4 in the system Si_3N_4-C-N_2 (1 atm) was determined to be 1839 C ± 14 C. A brief discussion is given regarding β-Si_3N_4 crystals that formed during the decomposition experiments.

224. **Inomata, Y., Matsuyama, T., Yukino, K., and Tsutsumi, M., "Microstructure and Etching of Hot Pressed Silicon Nitride with Aluminum Oxide", Yogyo Kyokai Shi, 84, 304-305 (1976).**

Study of microstructure of hot-pressed material comprising 70 w/o Si_3N_4 and 30 w/o Al_2O_3. Structure consisted of β or β' grains bridged with x-phase or glass. β to β' transformation proceeds by solution precipitation.

225. **Inomata, Y., and Uemura, Y., "Nitridation of Kinetics of Silicon Powder", Yogyo Kyokai Shi, 83, 244-248 (1975). (In Japanese)**

Nitridation kinetics on high purity, 2 μm Si powder were linear. The observed activation energy of 158 kcal/mol and rate dependence upon square root of particle size indicate that diffusion of N through a Si_3N_4 product layer is rate-controlling. Reaction proceeds through repeated cracking or exfoliation of Si_3N_4 layer.

226. **Iskoe, J. L., Lange, F. F., and Diaz, E. S., "Effect of Selected Impurities on the High Temperature Mechanical Properties of Hot-Pressed Silicon Nitride", J. Mater. Sci., 11, 908-912 (1976).**

α- and β-Si_3N_4 powders containing selected impurities and 5 w/o MgO were hot pressed to full density. Use of the former powder gave higher strength. CaO and alkaline oxides reduced high temperature strength but Fe_2O_3 and Al_2O_3 had no apparent effect.

227. **Jack, K. H., "Nitrogen Ceramics", Trans. J. Brit. Ceram. Soc., 72, 376-384 (1973).**

Summarizes crystal structure, fabrication, and properties of "sialon" materials and other Si-M-O-N ceramics where M = Al, Li, Mg, Ga, or Be.

228. **Jack, K. H., "Review: Sialons and Related Nitrogen Ceramics", J. Mater. Sci., 11, 1135-1158 (1976).**

"Sialons" and other nitrogen ceramics offer better prospects for technological exploitation than Si_3N_4. Structures, phase relationships, and properties of these new oxynitrides are reviewed.

229. **Jack, K. H., and Wilson, W. I., "Ceramics Based on the Si-Al-O-N and Related Systems", Nature Phys. Sci. (London), 238, 28-29 (July 10, 1972).**

Announcement of development of "sialon" materials such as β-Si_3N_4 containing up to 60% Al_2O_3. Resulting β-material has the desirable properties of Si_3N_4 and is easier to fabricate.

230. **Jayatilaka, A. deS., and Leake, J. A., "The Influence of Progressive Oxidation on the Fracture Toughness and Strength of Reaction-Bonded Silicon Nitride at Elevated Temperature in Air", Proc. Brit. Ceram. Soc., No. 25, 311-323 (1975).**

Reaction-bonded Si_3N_4 prepared from pure (98%) Si powder was tested at room temperature and at temperatures up to 900 C after heating in air for up to 9 hours. Results show that the small increase in K_{Ic} is due partly to oxidation and partly to microplasticity at the crack tip. High temperature modulus of elasticity decreased with increasing temperature but the room temperature modulus increased for specimens held for long periods at high temperature. The modulus of rupture decreased with both increasing temperature and longer times at high temperature.

231. **Jayatilaka, A. deS., Page, T. F., and Leake, J. A., "Scanning Electron Microscopy of Reaction-Sintered Silicon Nitride", J. Mater. Sci., 9, 514-515 (1974).**

Etching of polished sections of reaction-sintered Si_3N_4 in 40% HF left material that was mainly β-Si_3N_4. Some hexagonal β-Si_3N_4 crystals had hollow cores.

232, **Jelacic, C., and Dervisbegovic, H., "Étude sur quelques particularités de la synthèse du silicium nitride", Bull. Soc. Fr. Ceram., No. 105, 17-33 (1974).**

Discusses the effects of solid and gas impurities on nitridation of Si.

233. **Jennings, H. M., and Richman, M. H., "Structure, Formation Mechanisms and Kinetics of Reaction Bonded Silicon Nitride", J. Mater. Sci., 11, 2087-2098 (1976).**

Models of nitridation are derived from microstructural observations and it is suggested that there are at least two independent nitridation mechanisms.

234. **Jennings, H. M., and Richman, M. H., "The Use of Microscopy for Determining the Formation Mechanism of Beta-Silicon Nitride", Elektronmikroskopiever Suidelike Afr., 5, 117-118 (1975).**

The crystallization of β-Si_3N_4 in Si powder heated in N atmosphere at 1350-1450 C was studied. A shell of Si_3N_4 forms on the surface and then spikes penetrate into th Si grains. The spikes grow together into a single grain with many dislocations. The reaction rate is linear.

235. **Jeyes, J. A., Lines, D J., and Manton, S. M., "The Engineering of Hot-Pressed Silicon Nitride for Gas-Turbine Applications", Proc. Brit. Ceram. Soc., No. 22, 377-389 (1973).**

Of the materials currently being evaluated for gas-turbine components, hot-pressed Si_3N_4 is attractive because of its low coefficient of thermal expansion, good thermal shock resistance, and high strength at elevated temperatures. Material developments for engineering applications must include increased fracture toughness, improved oxidation and creep resistance, and improvements in high temperature strength. Si_3N_4 materials must be developed to increase the Weibull modulus 'm' in order to provide a more consistent material.

236. **Jones, B. F., and Lindley, M. W., "The Influence of Hydrogen in the Nitriding Gas on the Strength of Reaction Sintered Silicon Nitride", J. Mater. Sci., 11, 1969-1971 (1976).**

Use of H in nitriding gas in flow system gives strength increase similar to that obtained by using static rather than flowing N.

237. **Jones, B. F., and Lindley, M. W., "Reaction Sintered Silicon Nitride. Part 2: The Influence of Nitrogen Gas Flow on Strength and Strength/Density Relationships", J. Mater. Sci., 11, 1288-1295 (1976).**

A "flow" nitriding system was used to study development of strength in reaction-sintered Si_3N_4. Material produced under "flow" conditions is notably weaker than that produced under "static" conditions. Low strengths obtained in nominally "static" experiments may be the result of unsuspected gas flow.

238. **Jones, B. F., and Lindley, M. W., "Strength, Density, Nitrogen Weight Gain Relationships for Reaction Sintered Silicon Nitride", J. Mater. Sci., 10, 967-972 (1975).**

Linear relationships were found between mean strength and N weight gain for isostatically-pressed Si compacts nitrided to weight gains of $<60\%$. For a given Si powder, the relationship depends upon the green density of the compact. A linear relationship that exists between mean strength and nitrided density is independent of green density for the compacts studied.

239. **Jones, B. F., and Lindley, M. W., "Additional Observations on the Strength/Nitrided Density Relationship for a Reaction Sintered Silicon Nitride", J. Mater. Sci., 11, 191-193 (1976).**

Extension of work reported in Entry No. 238.

240. **Jones, B. F., and Lindley, M. W., "Strength, Density and Nitrogen Weight Gain Relationships for Reaction Sintered Silicon Nitride Prepared from Fine Silicon Powders", Powder Met. Int., 8, 32-34 (1976).**

Linear relationships were found between mean strength and N weight gain for Si compacts made from two fine powders. Finer particle size powders have greater potential for producing high strength material than course powders.

241. **Kaiser, W., and Thurmond, C. D., "Nitrogen in Silicon", J. Appl. Phys., 30, 427-431 (1959).**

Liquid zones of Si were exposed to various gaseous ambients containing N and NH_3 in a floating zone apparatus. Concentration of N in Si near melting point if 10^{19} atoms per cm^3. Si_3N_4 precipitates from supersaturated liquid during cooling.

242. **Kamchatka, M. I., and Ormont, B. F., "Growth Kinetics of a Nitride Film During the Nitriding of Silicon by Ammonia at High Temperatures", Zh. Fiz. Khim., 45, No. 9, 2202-2205 (1971). (In Russian)**

The kinetics of interaction of NH_3 and a Si single crystal substrate were studied at 1350, 1300, 1250, 1200, and 1150 C. The isotherms of the rate of increase in film weight correspond to the equation: $h = 10^8(k/d) \log (t+1)$, where k is the reaction rate constant (g/cm^2-min), d is the density of Si_3N_4, viz. 3.18 g/cm^3, h is the thickness of the Si_3N_4 film in Å, and t is the time in minutes. The energy of activation was 57.8 kcal/mole.

243. **Kamiya, N., Oyama, Y., and Kamigaito, O., Yogyo Kyokai Shi, 83 (11), 553-557 (1975). (See Entry No. 465)**

244. **Kato, K., Inoue, Z., Kijima, K., Kawada, I., Tanaka, H., and Yamane, T., "Structural Approach to the Problem of Oxygen Content in Alpha Silicon Nitride", J. Amer. Ceram. Soc., 58, 90-91 (1975).**

The crystal structure of α-Si_3N_4 was investigated by an X-ray method using a single crystal specimen prepared by CVD. The O content, 0.5 ± 0.03%, was determined by 14 MeV neutron activation analysis. α-Si_3N_4 is essentially pure and not an oxynitride.

245. **Kato, A., and Ono, Y., "Synthesis of Ceramic Whiskers by Vapor-Phase Reaction. III. Growth of Silicon Nitride from the Vapor Phase", Nippon Kagaku Kaishi, No. 8, 1608-1610 (1973). (In Japanese)**

Growth of Si_3N_4 crystals in the $SiCl_4$ (or $SiCl_3H$)-H_2-N_2 system was studied at 1000-1760 C. Whiskers of α-Si_3N_4 grew more readily on a heated W filament than on a graphite substrate. At 1500-1600 C crystals had no branches but at >1700 C there was remarkable secondary growth. Deposition on a substrate at 1400-1500 C would be suitable for the growth of fibrous Si_3N_4 crystals from the vapor phase.

246. **Kato, A., Ono, Y., Kawazoe, S., and Mochida, I., "Finely Divided Silicon Nitride by Vapor Phase Reaction Between Silicon Tetrachloride and Ammonia", Yogyo Kyokai Shi, 80, 114-120 (1972). (In Japanese)**

Si_3N_4 produced by vapor phase reaction between $SiCl_2$ and NH_3 was examined by X-ray diffraction, IR spectroscopy, chemical analysis, and electron microscopy. The reaction produced amorphous products that slowly crystallized to α-Si_3N_4 with the evolution of excess N and H.

247. **Katz, R. N., and McLean, A. F., "Reaction-Bonded Silicon Nitride as a Small Gas Turbine Nozzle Material", Proc. Brit. Ceram. Soc., No. 22, 409-427 (1973).**

A total systems approach - design, materials processing and fabrication, materials properties, component test data, failure analysis, and NDT - is presented using a reaction-bonded Si_3N_4 nozzle (stator) of a small gas-turbine engine as an example. Emphasis is given to the design, testing, and failure analysis portion of the process and how these results are used to study the materials processing problems.

248. **Kieffer, R., Wruss, W., Gugel, E., and Feld, H., "Microstructures of Reaction Sintered Silicon Nitride", Prakt. Metallogr., 12, 225-233 (1975).**

Samples containing 80% α-Si_3N_4 were annealed at 1600 C for 2-16 hours in N. Fibers, 0.1-0.2 μm, formed in the pore space at <1600 C while at 1600 C thick columnar crystals formed. The latter crystals are not associated with the β-phase. α/β transformation is attributed to loss of O.

249. **Kiehle, A. J., Heung, L. K., Gielisse, P. J., and Rockett, T. J., "Oxidation Behavior of Hot-Pressed Si_3N_4", J. Amer. Ceram. Soc., 58, 17-20 (1975).**

Oxidation in air begins at 700-750 C with formation of amorphous SiO_2 and cristobalite. Formation of latter increases with temperature and Mg and Ca silicates form above 1000 C. Mg, Ca, and Fe lower oxidation resistance.

250. **Kijima, K., "Effect of the Oxygen Partial Pressure on the Growth Character of α-Si_3N_4", Yogyo Kyokai Shi, 83, 46-47 (1975).**

Increase of O partial pressure in preparation of Si_3N_4 by CVD gives polycrystals rather than single crystals.

251. **Kijima, K., Kato, K., Inoue, Z., and Tanaka, H., "Oxygen Content of α-Si_3N_4 Single Crystals", J. Mater. Sci., 10, 362-363 (1975).**

Results of O content analysis and structure determination on α-single crystals indicated the α-Si_3N_4 is a polymorph of Si_3N_4 and not an oxynitride, $S_{11.5}O_{0.5}N_{15}$.

252. **Kijima, K., Setaka, N., Ishii, M., and Tanaka, H., "Preparation of Si_3N_4 by Vapor-Phase Reaction", J. Amer. Ceram. Soc., 56, 346 (1973).**

Alpha-Si_3N_4 was formed by vapor-phase reaction in the system SiO_2-C-N_2. IR absorption profile shows band at $\sim$800 cm^{-1} identified as Si-N stretching.

253. **Kijima, K., Setaka, N., and Tanaka, H., "Preparation of Silicon Nitride Single Crystals by Chemical Vapor Deposition", J. Cryst. Growth, 24/25, 183-187 (1974).**

Si_3N_4 was prepared on graphite susceptors by chemical vapor deposition using a mixture of $SiCl_4$, H, and N gases. Prismatic single crystals of α-Si_3N_4 with hexagonal morphology were obtained. Felt-like fibers, whiskers, and thin plates of Si_3N_4 were also produced. The effect of temperature and N partial pressure on the character of the deposited material was studied in detail.

254. **Kijima, K., Tanaka, H., and Setaka, N., "Preparation of α-Silicon Nitride With Low Oxygen Impurity", Yogyo Kyokai Shi, 84, 14-19 (1976). (In Japanese)**

Prismatic single crystals of α-Si_3N_4 were prepared on graphite susceptors by vapor-phase reaction from a $SiCl_4$, N, and H gaseous mixtures. The α-Si_3N_4 crystals prepared were compared with those already reported and contained less O (0.05-0.09 w/o).

255. **Kirchner, H. P., and Seretsky, J., "Improving Impact Resistance by Energy-Absorbing Surface Layers", Bull. Amer. Ceram. Soc., 54, 591-592 (1975).**

Impact resistance of Si_3N_4 was improved by petalite surface layers but not by ZrO_2.

256. **Kirchner, H. P., Sotter, W. A., and Gruver, R. M., "Strengthening of Hot-Pressed Si_3N_4 by Heating and Quenching", J. Amer. Ceram. Soc., 58, 353 (1975).**

Quenching from 1350 C enhanced strength marginally.

257. **Kohatsu, I., and McCauley, J. W., "Re-Examination of the Crystal Structure of α-Si_3N_4", Mater. Res. Bull., 9, 917-920 (1974).**

Single crystal X-ray diffractometer data were used to refine the crystal structure of α-Si_3N_4. Bond length and site occupancy data do not indicate any O in the structure.

258. **Koide, K., Sugiura, K., and Mori, M., "Recent Silicon Nitride Refractories", Seramikkusu, 8, 816-823 (1973). (In Japanese)**

Review of nitride refractories and uses of Si_3N_4.

259. **Kolobova, K. K., Yakovleva, V. S., and Zakharov, E. L., "Determining the Oxygen Content in Partly Oxidized Silicon Nitride", Refractories, No. 3, 177-181 (1966). Translation of Ogneupory, No. 3, 52-55 (1966).**

The content of O (as oxynitride) in partially oxidized Si_3N_4 and in SiC refractories with a nitride and oxynitride bond were determined by the vacuum-extraction method.

260. **Komeya, K., "High-Density Silicon Nitride and Silicon Carbide", Seramikkusu, 10, 145-150 (1975). (In Japanese)**

The sintering of SiC and Si_3N_4 in the presence of oxides and elements is reviewed.

261. **Komeya, K., "Research and Development in Silicon Nitride", Kogyo Reametaru, 57, 68-72 (1974). (In Japanese)**

A review with 19 references.

262. **Komeya, K., and Inoue, H., "Synthesis of the α-Form of Silicon Nitride from Silica", J. Mater. Sci., 10, 1243-1246 (1975).**

α-Si_3N_4 was synthesized by reduction of SiO_2 in a N atmosphere using various thermal treatment conditions and compositions of SiO_2 and C. Optimum reaction conditions and products obtained are described.

263. **Komeya, K., and Noda, F., "Aluminum Nitride and Silicon Nitride for High Temperature Vehicular Gas Turbine Engines", Toshiba Rev., 13-18 (July-August 1974).**

Sintering behavior and other properties of Si_3N_4 and AlN bodies hot pressed with additives are reported as well as rotor testing results at room temperature using model turbine-like blades. Problems in using ceramics in turbines are also reviewed.

264. **Kopylova, V. P., and Nazarchuk, T. N., "Chemical Stability of Silicon Nitride and Oxynitride Powders", Sov. Powder Met. Metal Ceram., 14, 812-816 (1976). Translation of Porosh. Met., 14 (10), 38-43 (1975).**

Data on reactions of Si_3N_4 and Si_2ON_2 with acids and alkaline hydrozides. Si_2ON_2 is less stable than Si_3N_4.

265. **Kossowsky, R., "Cyclic Fatigue of Hot-Pressed Si_3N_4", J. Amer. Ceram. Soc., 56, 531-535 (1973).**

Cyclic fatigue behavior of two grades of hot-pressed Si_3N_4 was investigated. Flat, cantilever type specimens (5½" x 1"), loaded by an eccentric driver rotating at 1800 rpm, were tested at temperatures up to 1300 C. Lifetime of low purity material was controlled by stress corrosion at temperatures ≤1200 C. Above that temperature plastic deformation was rate controlling for both materials.

266. **Kossowsky, R., "The Microstructure of Hot-Pressed Silicon Nitride", J. Mater. Sci., 8, 1603-1615 (1973).**

Replica and thin foil transmission microscopy, X-ray diffraction, microprobe and Auger analyses were used to investigate the grain morphology, distribution of impurities and inclusions, phase and dislocation structures of commercial hot-pressed Si_3N_4. High concentrations of impurities, e.g., Ca, were detected at grain boundaries. Low density Si_3N_4 inclusions degraded strength. Correlations among strength, densification, and distribution of elements and phases are considered.

267. **Kossowsky, R., "Wetting of Silicon Nitride by Alkaline-Doped $MgSiO_3$", J. Mater. Sci., 9, 2025-2033 (1974).**

Alkaline oxide additions improve wetting of Si_3N_4 by $MgSiO_3$. Hot pressing of Si_3N_4 occurs via liquid-phase sintering. Alkaline impurity level should be <50-100 ppm for optimum strength.

268. **Kossowsky, R., Miller, D. G., and Diaz, E. S., "Tensile and Creep Strengths of Hot-Pressed Si_3N_4", J. Mater. Sci., 10, 983-997 (1975).**

Tensile, creep, and stress-rupture data for two commercial hot-pressed Si_3N_4 materials are presented. Strength is controlled by the grain-boundary glassy phase and deformation, at temperatures >1000 C, is controlled by grain-boundary sliding. A model based on the concept of geometrically necessary wedge cracks accounts for the observed effects of strain rate, stress, temperature environment, and impurity content. These materials are creep strain limited.

269. **Krasotkina, N. I., "Stability of Silicon Nitride Heated in Air and in Carbon Monoxide", Refractories, No. 6, 367-372 (1967). Translation of Ogneupory, No. 6, 33-39 (1967).**

Si_3N_4 oxidizes in air at 1100-1500 C mainly with the formation os SiO_2 and addition of NaF contributes to formation of Si_2ON_2. In a CO atmosphere the additions of CaF_2 and MgO also contribute to the formation of Si_2ON_2 at 1550 C.

270. **Lamure, J., and Billy, M., "Nitrogen Determination of Silicon Nitride", Compt. rend., 245, 1931-1933 (1957). (In French)**

The action of N on Si at high temperatures yields orthorhombic Si_3N_4, as determined by X-ray identification. Nitrides, Si_2N_3 and SiN, do not form. The Si_3N_4 is not attacked by alkaline washings but is attacked with difficulty by H_2SO_4, concentrated HF, or fused carbonates. Si and N may be determined by attack in VACUO with PbO or Na_2O_2.

271. **Lange, F. F., "Crack Extension and Arrest in Contact Stress Fields", Int. J. Fract., 12, 409-417 (1976).**

Experimental observations for hot-pressed Si_3N_4 and SiC are presented to examine the crack size effect and its predicted relation to materials problems.

272. **Lange, F. F., "Effect of Microstructure on the Strength of Si_3N_4 - SiC Composite System", J. Amer. Ceram. Soc., 56, 445-450 (1973).**

SiC dispersions of average particle size 5, 9, and 32 μm were used to form hot-pressed composites with Si_3N_4. Strength of the two larger particle dispersions was controlled by crack size. Strength of fine particle dispersion was controlled by both fracture energy and elastic modulus. Several of the composites appear promising as high-temperature structural materials.

273. **Lange, F. F., "High-Temperature Strength Behavior of Hot-Pressed Si_3N_4: Evidence for Subcritical Crack Growth", J. Amer. Ceram. Soc., 57, 84-87 (1974).**

High-temperature strength of commercial hot-pressed Si_3N_4 was investigated. Results indicate that strength degradation and sensitivity of high-temperature strength to stressing rate is attributed to subcritical crack growth caused by stress-enhanced grain boundary sliding at the crack front. The susceptibility to crack growth increases with increasing impurity content (i.e., Ca) and increasing temperature. The viscosity of the boundary phase greatly influences the high-temperature mechanical behavior.

274. **Lange, F. F., "Relation Between Strength, Fracture Energy, and Microstructure of Hot-Pressed Si_3N_4", J. Amer. Ceram. Soc., 56, 518-522 (1973).**

A fracture mechanics approach was used to study the hot-pressing behavior and mechanical properties of Si_3N_4. High strength of material fabricated from high α-Si_3N_4 powder relates to high fracture energy, the latter being attributed to the presence of elongated grains.

275. **Lange, F. F., and Terwilliger, G. R., "The Powder Vehicle Hot-Pressing Technique", Bull. Amer. Ceram. Soc., 52, 563-565 (1973).**

Hot-pressing technique using a powder vehicle as a pressure transmitting medium is described. A 70% dense reaction-sintered Si_3N_4 turbine blade was densified to 98% of theoretical. Pressure transfer and effect of surface geometry on shape are discussed.

276. **Leimer, G., and Gugel, E., "Infiltration - Verbundwerkstoffe auf der Basis von Siliziumnitrid", Z. Metallk., 66, 570-576 (1975).**

An attempt was made to densify the porous reaction-sintered Si_3N_4 by means of infiltration which only succeeded with so-called de-oxidation alloys which react with Si_3N_4. The phases, structures, and mechanical properties of the best of these composites are reported.

277. **Lin, S-S., "Mass Spectrometric Analysis of Vapors in Oxidation of Si_3N_4 Compacts", J. Amer. Ceram. Soc., 58, 160 (1975).**

Atmospheric pressure sampling and mass spectrometry were used to analyze the vapor constituents of the oxidation over Si_3N_4 compacts at 1000, 1200, and 1400 C. The gases observed were NO and N, no SiO was detected. The oxidation of Si_3N_4 yields SiO_2 and NO followed by the dissociation of NO into N and O.

278. **Lin, S-S., "Mass Spectrometric Analysis of Vapor in Oxidation in Si_2ON_2", J. Amer. Ceram. Soc., 59, 273-274 (1976).**

Vapor species generated from the oxidation of Si_2ON_2 were examined by mass spectrometric and atmospheric pressure sampling techniques. The oxidation yields No and N but not SiO. The process is similar to the oxidation of Si_3N_4 in which NO is a major product which subsequently dissociates.

279. **Lin, S-S., "Mass Spectrometric Studies of the Nitridation of Silicon", J. Amer. Ceram. Soc., 58, 271-273 (1975).**

The nitridation of Si was examined by analyzing the atmosphere with a mass spectrometer. SiO vapor was found throughout the entire temperature range in the order of 10^{-3} of the volume of the nitriding agent. Controversial results obtained in previous investigations are explained in terms of the SiO vapor and the O partial pressure of the system. The effects of H and H_2O on nitridation are also discussed.

280. **Lindley, M. W., and Godfrey, D. J., "Silicon Nitride Ceramic Composites with High Toughness", Nature, 229, 192-193 (1971).**

Fiber reinforcement of Si_3N_4 is a possible solution to the brittleness problem which limits the use of ceramic materials in engineering. Mechanical property data presented for Si_3N_4/SiC fiber composites show the capability of increasing the fracture toughness of Si_3N_4 by fiber additions.

281. **Lindop, T. W., "Engineering Ceramics Abroad. Silicon Nitride. Promising Material for Replacing Heat-Resistant Metals", Kinzoku, 42, 42-48 (1972). (In Japanese)**

Development, manufacture, properties, and applications of Si_3N_4 are reviewed.

282. **Lindop, T. W., "Engineer's Guide to Silicon Nitride", Mater. Eng., 75 (1), 28-31 (1972).**

Review of the fabrication processes and engineering properties of reaction-sintered Si_3N_4.

283. **Lotholary, P., Goursat, P., Tetard, D., and Billy, M., "Silicon-Oxygen-Nitrogen System: II, Corrosion of Si_2N_2O Powder in Oxygen at >1100 C", Rev. Int. Hautes Temp. Refract., 9, 325-331 (1972). (In French)**

The oxidation resistance of Si_2N_2O powders was studied at 16-135 torr and >1100 C. Two successive processes, interfacial (activation energy 43 kcal/mol) and diffusional (activation energy 36 kcal/mol), control the kinetics of the oxidation reaction. The reaction rate is almost independent of O pressure except initially when O absorption is the main process.

284. **Lumby, R. J., and Coe, R. F., "The Influence of Some Process Variables on the Mechanical Properties of Hot-Pressed Nitride", Proc. Brit. Ceram. Soc., No. 15, 91-101 (1970).**

A fully instrumented experimental hot-pressing system is described in which the temperature and pressure application are reproducibly controlled and the densification of powder is continuously recorded. The equipment has been used to study the effects of process variables on the densification of all α-Si_3N_4 pressed at 1700-1750 C. Effects of same variables were examined with respect to modulus of rupture measured at room temperature. Time at temperature has a pronounced effect - some electron micrograph evidence is given.

285. **Mangels, J. A., "Effect of H_2-N_2 Nitriding Atmospheres on the Properties of Reaction-Sintered Si_3N_4", J. Amer. Ceram. Soc., 58, 354-355 (1975).**

Addition of H to the nitriding atmosphere altered the grain structure and grain-boundary composition of Si_3N_4, improving both the room-temperature and high-temperature physical properties.

286. **Marchand, R., Laurent, Y., and Lang, J., "Structure of α-Silicon Nitride", Acta Cryst., B 25, 2157-2160 (1969). (In French, Summary in English)**

X-ray data show α-Si_3N_4 unit cell of P31c symmetry (a = b =7.765, c = 5.622 Å) contains four formula units. Structure was refined to R = 8.6% for non-zero data. The sequence of the planes containing Si atoms is ABCD.

287. **Maruyama, T., and Suzuki, H., "Young's Modulus of Silicon Nitride Fibers", J. Amer. Ceram. Soc., 58, 532-533 (1975).**

Young's modulus for Si_3N_4 ceramic fibers was determined by flexural vibration technique. Removal of surface silica changed E values from 1.52-2.21 to 2.51-2.98 dynes/cm^2.

288. **Mary, J. P., Lotholary, P., Goursat, P., Billy, M., and Mexmain, J., "Realisation de pieces ceramiques en oxyniture de silicium par frittage classique", Bull. Soc. Fr. Ceram., No. 105, 3-9 (1974).**

Investigated were effects of heat treatment, atmosphere, and particle character on sintering. Al_2O_3 and MgO promote densification. High densities can be obtained and a liquid phase sintering mechanism is proposed.

289. **Masaki, H., Oyama, Y., and Kamigaito, O., "Low Temperature Synthesis of Silicon Nitride Solid Solution", Jap. J. Appl. Phys. 14, 301-302 (1975).**

α-Si_3N_4 solid solution was formed by nitriding Si powder with AlN and/or Al_2O_3 in a N-H atmosphere at 1200-1400 C. Lattice spacings and intensities are given for α-Si_3N_4 and for the new solid solution.

290. **Matkin, D. I., Denton, I. E., Valentine, T. M., and Warrington, P., "Fabrication of Silicon Nitride by Ceramic/Plastic Technology", Proc. Brit. Ceram. Soc., No. 22, 291-304 (1973).**

A ceramic/plastic forming route, warm molding, has been developed and used for the fabrication of reaction-bonded Si_3N_4. This technique makes it possible to fabricate complex shaped ceramic components at medium production rates, with high density, high fracture strength, and good as-fired surface finishes.

291. **Mazdiyasni, K. S., and Cooke, C. M., "Consolidation, Microstructure, and Mechanical Properties of Si_3N_4 Doped with Rare-Earth Oxides", J. Amer. Ceram. Soc., 57, 536-537 (1974).**

Additions of ~2.5 at/o rare-earth oxides as Ce_2O_3, CeO_2, CeH_3, and especially CeN yield Si_3N_4 with high density (98-99.9% theoretical) and improved thermomechanical properties. Data are included on microstructure, oxidation, and high-temperature creep.

292. **Mazdiyasni, K. S., and Cooke, C. M., "Synthesis, Characterization, and Consolidation of Si_3N_4 Obtained from Ammonolysis of $SiCl_4$", J. Amer. Ceram. Soc., 56, 628-633 (1973).**

Very high-purity, fine-particle-size, amorphous Si_3N_4 powders were produced by thermal decomposition of $Si(NH)_2$ in vacuum. The powder gradually transformed to α-Si_3N_4 at temperatures $\leqslant$1450 C, and to β-Si_3N_4 at higher temperatures. Hot-pressing parameters, chemical etching, and dielectric property measurements are discussed.

293. **McHenry, K. D., Yonushonis, T., and Tressler, R. E., "Low-Temperature Sub-Critical Crack Growth in SiC and Si_3N_4", J. Amer. Ceram. Soc., 59, 262-263 (1976).**

Double-torsion technique was used to study slow crack growth in Si_3N_4. Stress intensity data are given for several environments at temperatures near ambient.

294. **McLean, A. F., "Ceramics in Automotive Gas Turbines", Bull. Amer. Ceram. Soc., 52, 464-466, 482 (1973).**

Review of status of ceramic materials with potential for turbine applications. Si_3N_4 and SiC have good high-temperature properties and show promise for low cost forming techniques. Development of design technology for these materials is discussed.

295. **Mehan, R. L., and McKee, D. W., "Interaction of Metals and Alloys with Silicon-Based Ceramics", J. Mater. Sci., 11, 1009-1018 (1976).**

The reaction products formed by the reaction of metals and alloys with Si-based ceramics in air at temperatures ~1000 C after 100 hours were silicides, silicates, and carbides. The severity of the interaction depended on temperature and the ease of migration of free Si from the ceramic part to the metallic phase. These reactions may be deleterious in applications in which the ceramics and metals are in contact for extended periods at high temperature.

296. **Messier, D. R., and Gazza, G. E., "Thermal Decomposition of Al_2O_3-Si_3N_4 Mixtures", J. Amer. Ceram. Soc., 58, 538-540 (1975).**

Weight losses of up to 20% were found on Si_3N_4 powders milled in Al_2O_3 and heated in N at 1450 C. Kinetics and thermodynamics of possible decomposition reactions are discussed.

297. **Messier, D. R., and Wong, P., "Kinetics of Nitridation of Si Powder Compacts", J. Amer. Ceram. Soc., 56, 480-485 (1973).**

The kinetics of the reaction of Si powder compacts and N to form Si_3N_4 were investigated thermogravimetrically from 1300-1450 C. The results indicate that trace amounts of O inhibit the rate of nitridation by forming a thin protective layer of SiO_2, whereas Fe impurities catalytically accelerate the rate of reaction by liquid-phase formation. Complicating factors that account for difficulties in interpreting the reaction kinetics and for the poor agreement among previous investigations are discussed.

298. **Messier, D. R., Wong, P., and Ingram, A. E., "Effect of Oxygen Impurities on the Nitridation of High-Purity Silicon", J. Amer. Ceram. Soc., 56, 171-172 (1973).**

It is shown that O impurities at levels considerably <10 ppm can significantly retard the rate of nitridation of Si powder compacts. Outgassing and the use of a suitable getter enhance the rate of nitridation.

299. **Mitomo, M., "Effect of Oxygen Partial Pressure of Nitridation of Silicon", J. Amer. Ceram. Soc., 58, 527 (1975).**

The effect of O partial pressure on the amount of Si nitrided was small but with decreasing O pressure the amount of β-phase increased and the α-phase decreased.

300. **Mitomo, M., "Pressure Sintering of Si_3N_4", J. Mater. Sci., 11, 1103-1107 (1976).**

Si_3N_4 was hot pressed with 5% MgO at 1450-1900 C under N pressure. Maximum density obtained was 95% of the theoretical value. The sintering process was inferred to be liquid-phase divided into two processes: rearrangement and solution precipitation. Rearrangement contributed ~10% and solution precipitation the remaining 17% of densification.

301. **Mitomo, M., Oshima, C., and Tsutsumi, M., "Microstructural Change During Gas Pressure Sintering of Silicon Nitride", Yogyo Kyokai Shi, 84, 356-360 (1976). (In Japanese)**

Density of 95% of theoretical was obtained by gas-pressure sintering of Si_3N_4 with 5% MgO at 10 atm N and 1800 C. Densification was attributed to rearrangement at <1500 C and solution precipitation at higher temperature.

302. **Mitomo, M., and Sharp, J. H., "Oxidation of α- and β-Silicon Nitride", Yogyo Kyokai Shi, 84, 33-36 (1976).**

α-Si_3N_4 had a lower oxidation resistance than β-Si_3N_4 and the activation energies for each phase were similar. The results fitted a parabolic rate law and O diffusion in cristobalite was inferred to be the rate determining process.

303. **Mitomo, M., Tanaka, H., and Tanaka, J., "The Synthesis of α-Si_3N_4", Yogyo Kyokai Shi, 82, 144-145 (1974). (In English)**

Structurally pure α-Si_3N_4 was obtained by the thermal decomposition, at temperatures up to 650 C, of $Si(NH)_2$ prepared by bubbling NH_3 into cooled $SiCl_4$. From a thermodynamic point of view the incorporation of O into Si_3N_4 is inevitable and the reasons are shown.

304. **Mitomo, M., Tsutsumi, M., Bannai, E., and Tanaka, T., "Sintering of Si_3N_4", Bull. Amer. Ceram. Soc., 55, 313 (1976).**

Si_3N_4 powder containing 5% MgO was sintered to >90% of theoretical density at 1700 C in N at 10 atmospheres.

305. **Morgan, P.E.D., "Comment on 'Reaction of Si_3N_4 with Al_2O_3 and Y_2O_3' and 'Silicon Yttrium Oxynitrides' by R. R. Wills", J. Amer. Ceram. Soc., 59, 86 (1976).**

Discussion regarding agreement of Wills' data with theory of isomorphous replacements of ions in oxynitride structures. (See Entry Nos. 398 and 399)

306. **Mosher, D. R., Raj, R., and Kossowsky, R., "Measurement of Viscosity of the Grain-Boundary Phase in Hot-Pressed Silicon Nitride", J. Mater. Sci., 11, 49-53 (1976).**

The viscosity of the grain-boundary amorphous phase in commercial hot-pressed Si_3N_4 was measured by an internal friction technique. The viscosity in the region of the glass transition (850-900 C) was $\sim 5 \times 10^{15}$ P/cm of the grain boundary, with an apparent activation energy of 163 kcal mol^{-1}.

307. **Motoi, S., and Hidaka, S., "Synthesis of Silicon Nitride from Silica", Denki Kagaku Oyobi Kogyo Butsuri Kogaku, 43 (1), 33-38 (1975). (In Japanese)**

High-temperature reaction of SiO_2 and N in the presence of C was used to prepare Si_3N_4. Formation of Si_3N_4 started at 1300 C and was complete by 1550 C without any formation of liquid Si. The highest yield was attained when the mole ratio $C/SiO_2 = 2.6$.

308. **Mukaseev, A. A., Gribkov, V. N., Shchetanov, B. V., Isaikin, A. S., and Silaev, V. A., "Normal Modulus of Elasticity of Silicon Nitride Whiskers", Soviet Powder Met. Metal Ceram., 11 (3), 245-246 (1972). Translation of Porosh. Met., 11 (3), 97-98 (1972).**

Measurements were made by ultrasonic technique of the normal modulus of elasticity of α-Si_3N_4 whiskers of three crystallographic orientations: $E_{5\ K<0001>} = 47{,}930$, $E_{<1\bar{2}12>} = 38{,}530$, and $E_{<2\bar{4}21>} = 49{,}750$ kg/mm^2.

309. **Narita, K., and Mori, K., "Crystal Structures of Silicon Nitride", Bull. Chem. Soc. Jap., 32, 417-419 (1959). (In English)**

Short communication on investigations of α- and β-Si_3N_4 by X-ray and electron diffraction. Diffraction patterns were indexed and lattice parameters determined.

310. **Naruse, W., Nojiri, M., and Tada, M., "Formation Conditions and Properties of the Two Crystal Phases of Silicon Nitride", Nippon Kinzoku Gakkaishi, 35 (8), 731-738 (1971). (In Japanese, figure captions in English)**

Alpha- and beta-Si_3N_4 coexist in different proportion s depending on nitriding conditions. In general, α-Si_3N_4 formed on the surface of the piece during nitriding, and β-Si_3N_4 formed in the center. Temperatures below 1200 C and above 1300 C promoted the growth of α-Si_3N_4 and β-Si_3N_4 respectively. The finer the particle size and the lower the purity of the Si powder, the more α-Si_3N_4 formation is favored. Articles of α- β-Si_3N_4 powders were pressed under the same conditions and sintered in N at 1400-1800 C for three hours. Porosities and mechanical strength were measured in relation to sintering temperature and pressing pressure.

311. **Niihara, K., and Hirai, T., "Chemical Vapour-Deposited Silicon Nitride. Part I - Preparation and Some Properties", J. Mater. Sci., 11, 593-603 (1976).**

Pyrolytic Si_3N_4 was deposited on graphite substrates, using a mixture of $SiCl_4$, NH_3, and H_2. The effect of deposition conditions on some properties of the deposited products and the dependence of formation of amorphous or crystalline deposits on deposition temperature and total pressure were investigated. The surface and cross-sectional structures showed growth cones and oriented crystals which are strongly dependent on the deposition conditions. No segregation of N or Si at the cone boundaries was found.

312. **Niihara, K., and Hirai, T., "Chemical Vapour-Deposited Silicon Nitride. Part 2 - Density and Formation Mechanism", J. Mater. Sci., 11, 604-611 (1976).**

CVD Si_3N_4 (pyrolytic Si_3N_4) has been prepared from a $SiCl_4 + NH_3/H_2$ system at 1100-1500 C under total pressures of 5 to 300 torr. The densities of the crystalline deposits are 3.15 to 3.18 g cm^{-3} and almost independent of the deposition conditions, while the densities of amorphous deposits depend strongly on the deposition conditions, having a minimum value of 2.60 g cm^{-3} at 1200 C and 40 torr. The deposition rate of the Py-Si_3N_4 obeys a linear law and has activation energies of formation 30 to 33 and 53 kcal mol^{-1} for the amorphous and crystalline deposits respectively.

313. **Nojiri, M., "Development and Use of Silicon Nitride", Kinzoku, 40, 49-52 (1970). (In Japanese)**

Review of manufacturing methods, properties, and applications of Si_3N_4. Structural, refractory, electrical insulating, abrasive, and coating applications are considered.

314. **Nomata, Y., and Inoue, Z., Yogyo Kyokai Shi, 81, 441-444 (1973). (See Entry No. 508)**

315. **Nuttall, K., and Thompson, D. P., "Observations on the Microstructure of Hot-Pressed Silicon Nitride", J. Mater. Sci., 9, 850-853 (1974).**

The microsturucture of β-Si_3N_4 produced by hot pressing 93% α-Si_3N_4 powder with 5 w/o MgO was examined by replica and thin foil techniques. The β-Si_3N_4 exhibited preferred orientation and evidence was found for the presence of an amorphous phase.

316. **Osborne, N. J., "Creep Testing of High Temperature Engineering Ceramics", Proc. Brit. Ceram. Soc., No. 25, 263-280 (1975).**

Creep testing was carried out at 1227 C and 77 MN/m^2 and at 1370 C and 77 MN/m^2 on commercial hot-pressed Si_3N_4 materials and a range of hot-pressed sialon research materials. Data on the modulus of rupture strength at room temperature, 1200 C, and 1370 C and on oxidation resistance at 1370 C are included.

317. **Osipova, I. I., and Pogorelova, D. A., "Recrystallization of Silicon Nitride During Hot Pressing", Sov. Powder Met. Metal Ceram., 14, 1015-1017 (1975). Translation of Porosh. Met., 14 (12), 74-77 (1975).**

Recrystallization processes in a Si_3N_4-base material containing Si_3N_4 , 5% MgO hot pressed at 1600-1700 C were studied by metallurgical and electron microscopy. Results showed the grain size decreased as a result of hot pressing.

318. **Oyama, Y., "Solid Solution in the Ternary System, Si_3N_4-AlN-Al_2O_3", Jap. J. Appl. Phys., 11, 750-751 (1972). (In English)**

X-ray diffraction studies of sintered powdered mixtures were used to show that AlN is in a substitutional solid solution in Si_3N_4-AlN-Al_2O_3 system and that the solubility limit is mainly determined by vacancy density.

319. **Oyama, Y., "Solid Solution in the Ternary System, Si_3N_4-Al_2O_3-Ga_2O_3", Jap. J. Appl. Phys., 11, 1572 (1972). (In English)**

Solid solution in the system was of the type $Si_3N_{4s.s.}$ (Al_2O_3-Ga_2O_3). A tentative phase diagram is given.

320. **Oyama, Y., and Kamigaito, O., Yogyo Kyokai Shi, 80, 29-38 (1972). (See Entry No. 509).**

321. **Oyama, Y., and Kamigaito, O., Yogyo Kyokai Shi, 80, 327-336 (1972). (See Entry No. 509)**

322. **Oyama, Y., and Kamigaito, O., "Sintered Silicon Nitride - Magnesium Oxide System", Yogyo Kyokai Shi, 81, 290-293 (1973). (In Japanese)**

Studies were made on sintered Si_3N_4 with MgO added and hot pressed at 1730 C. At low concentrations of MgO only β-Si_3N_4 was observed, as MgO concentrations increased $MgSiN_2$ was formed, and, later, $2MgOSiO_2$. Solubility limit of MgO in β-Si_3N_4 is estimated to be 30% at 1730 C. Enhanced sintering of β-Si_3N_4 with MgO is attributed to diffusion of Si vacancies.

323. **Oyama, Y., and Kamigaito, O., "Solid Solubility of Some Oxides in Si_3N_4", Jap. J. Appl. Phys., 10, 1637 (1971). (In English)**

X-ray diffraction analysis and electron probe microanalysis showed the presence of a new phase in mixtures of Si_3N_4, α-Al_2O_3, and Li_2CO_3 powders compacted at 1750 C. The new phase is a solid solution comprising Si_3N_4-Al_2O_3 or Si_3N_4-Li_2O-Al_2O_3.

324. **Paluszny, A., "Design with Brittle Materials", Mater. Sci. Eng., 15, 39-50 (1974).**

The general design philosophy and methods used in the design of ceramic turbine stators and rotors are discussed. Test results on Si_3N_4 components are presented.

325. **Parker, A., and Healy, C., "The Determination of Nitrogen in Silicon Nitride", Analyst (London), 95, 204-206 (1970).**

A method for the determination of N in Si_3N_4 in which the nitride is dissolved in a mixture of HF contained in a closed vessel lined with PTFE. The NH_3 formed after dissolution at 150 C overnight (at least seven hours) is steam distilled from an alkaline solution and determined by titration. The coefficient of variation is ∿1.0%.

326. **Parr, N. L.,"Silicon Nitride, A New Ceramic for High Temperature Engineering and Other Applications", Research (London), 13, 261-269 (1960).**

Review of preparation and properties of reaction-bonded Si_3N_4. Duplex structure is described. Properties discussed include density, bend strength, creep, hardness, thermal expansion, elastic modulus, and oxidation resistance.

327. **Parr, N. L., "Silicon Nitride", Materials for Engineers Series", The Engineer, 222, 18-19 (July 1, 1966).**

Si_3N_4 is presented as one of the new, hard, inorganic nonmetallic materials as having possible engineering applications. Si_3N_4 responds to normal manufacturing processes and possesses good thermal shock resistance. It is available in the form of (1) theoretical density material with transverse rupture strength of the order of 100,000 psi, (2) porous, permeable and non-permable bodies, (3) whisker wool. Production routes and design considerations are explained. A compact chart reviewing the properties and suppliers of Si_3N_4 is provided.

328. **Parr, N. L., and May, E.R.W., "The Technology and Engineering Applications of Reaction-Bonded Silicon Nitride", Proc. Brit. Ceram. Soc., No. 7, 81-98 (1967).**

Recent experience in production methods, physical properties, and current experimental applications of reaction-bonded Si_3N_4 bodies are described. Applications are aimed at establishment of an appropriate design philosophy to exploit the unusual properties obtained in this material.

329. **Parr, N. L., Sands, R., Pratt, P. L., May, E.R.W., Shakespeare, C. R., and Thompson, D. S., "Structural Aspects of Silicon Nitride", Powder Met., No. 8, 152-163 (1961).**

Describes experiments to establish the conditions under which α- and β-Si_3N_4 may be produced independently or in varying proportions. Suggests a method for varying the properties of Si_3N_4 by incorporating a dispersion or continuous network of other elements and compounds.

330. **Pehlke, R. D., and Elliott, J. F., "High Temperature Thermodynamics of the Silicon, Nitrogen, Silicon-Nitride System", Trans. AIME, 215, 781-785 (1959).**

The equilibrium pressure of N gas over pure Si metal and Si_3N_4 was measured in temperature range 1400-1700 C. From the experimental data, the standard free energies and enthalpies of formation of α-Si_3N_4 have been calculated as functions of temperature over this range. Specific heat, molar enthalpy, molar entropy, standard enthalpy of formation, and standard free energy of formation are estimated for the temperature range 298-1400 C.

331. **Petrovic, J. J., Dirks, R. A., Jacobson, L. A., and Mendiratta, M. G., "Effects of Residual Stresses on Fracture from Controlled Surface Flaws", J. Amer. Ceram. Soc., 59, 177-178 (1976).**

Effects of surface removal and annealing on flaws in and stress intensity factors of hot-pressed Si_3N_4.

332. **Petrovic, J. J., Jacobson, L. A., Talty, P. K., and Vasudevan, A. K., "Controlled Surface Flaws in Hot-Pressed Si_3N_4", J. Amer. Ceram. Soc., 58, 113-116 (1975).**

Surface flaws of controlled size and shape were produced in high-strength hot-pressed Si_3N_4 with a Knoop microhardness indenter. Fracture was initiated at a singly suitably oriented flaw on the tensile surface of a four-point bend specimen. The stress required to propagate the controlled flaw was used to calculate stress-intensity factor, K_{Ic}. Effects of annealing and slow crack growth at high temperatures are also discussed.

333. **Petrovic, J. J., and Mendiratta, M. G., "Mixed-Mode Fracture from Controlled Surface Flaws in Hot-Pressed Si_3N_4", J. Amer. Ceram. Soc., 59, 163-167 (1976).**

The room temperature mixed-mode fracture of commercial hot-pressed Si_3N_4 was examined using controlled surface flaws in four-point bending. Catastrophic fracture paths were non-coplanar with the initial flaw plane, and stress intensity factor ratio K_I/K_{Ic} was <1 for fracture in modes II and III. A non-coplanar maximum strain-energy release rate fracture criterion best described mixed-mode fracture.

334. **Pivinskii, Yu. E., Podobeda, L. G., Buravov, A. D., and Polubatonova, L. P., "Some Properties of Silicon Nitride Aqueous Suspensions", Sov. Powder Met. Metal Ceram., 15, 193-197 (1976). Translation of Porosh. Met., 15, (3), 37-42 (1976).**

Rheological properties of Si_3N_4 slips were examined as functions of solid-phase content and pH. Drying shrinkage of slip-cast articles was $<3\%$.

335. **Popper, P., and Ruddlesden, S. N., "The Preparation, Properties and Structure of Silicon Nitride", Trans. Brit. Ceram. Soc., 60, 603-626 (1961).**

The preparation of Si_3N_4 by heating pressed, extruded, or slip-cast Si powder in N and by other methods is described. The effects of temperature, atmosphere, and impurities on the rate of nitriding are considered: (1) the temperature must not be raised too quickly, (2) the presence of O can reduce the nitriding rate, (3) Fe_2O_3 and CaF_2 catalyze the reaction. The structures of the Si_3N_4 and of the fibers sometimes formed on nitriding Si are described.

336. **Popper, P., and Ruddlesden, S. N., "Structure of the Nitrides of Silicon and Germanium", Nature, 179, 1129 (1957).**

Preparation of Phase-I and Phase-II nitrides of Si and Ge are described. Phase-I can be indexed as orthorhombic and Phase-II as rhombohedral.

337. **Powell, B. D., and Drew, P., "The Identification of a Grain-Boundary Phase in Hot-Pressed Silicon Nitride by Auger Electron Microscopy", J. Mater. Sci., 9, 1867-1870 (1974).**

The intergranular amorphous phase in Si_3N_4 hot pressed with 7% MgO was identified, by Auger electron spectroscopy, as a glass having the estimated composition $(0.40 \pm 0.03)CaO \cdot (0.75 \pm 0.10)MgO \cdot 2SiO_2$. The rapid decrease in strength at temperatures >1000 C is attributed to the decrease in viscosity of this glass phase.

338. **Priest, H. F., Burns, F. C., Priest, G. L., and Skaar, E. C., "Oxygen Content of Alpha Silicon Nitride", J. Amer. Ceram. Soc., 56, 395 (1973).**

Pure α-Si_3N_4 was prepared by CVD and analyzed for O content. Five determinations showed $(0.30\% \pm 0.005\%)$ O with a standard deviation of 1.00%. The indexed X-ray pattern showed only α lines. Treatment at 1800 C and 275 psig N in a pressure furnace for several hours produced no conversion to β-Si_3N_4. It is concluded that α-Si_3N_4 is a stable, high temperature phase that does not require O for structural stability.

339. **Rabenau, A., "Silicon Nitride, A Ceramic Material for High Temperatures", Ber. Dtsch. Keram. Ges., 40, 6-12 (1963). (In German)**

Preparation and properties of Si_3N_4 are described. The reaction-sintering technique to produce articles of Si_3N_4 is treated in detail, followed by a review of the mechanical and physical properties of the material. Si_3N_4 can be used for high temperature applications. A review of the possible applications is given.

340. **Rabinowicz, E., "Grinding Damage of Silicon Nitride Determined by Abrasive Wear Tests", Wear, 39, 101-107 (1976).**

Si_3N_4 samples, surface ground to various depths, were measured using a technique developed for accurately determining the relative abrasive wear resistance. Resistance was lowered for a distance approximately equal to the depth of the cut, suggesting that care must be taken in the final finish operations to remove the surface damage introduced by earlier stages.

341. **Rae, D. M., "Silicon Nitride as a High Temperature Material", National Research Development Corporation Bulletin, No. 15, 4-10 (October 1959).**

A new material having excellent thermal shock and oxidation resistance and adequate creep strength at 1200 C was produced as a result of a search for stator blade materials for use in gas turbines at 1200 C. The best material was found to be Si_3N_4 stiffened with a fine dispersion of SiC. Reviewed are production methods, properties, and field trials in experimental gas turbines.

342. **Raider, S. I., Flitsch, R., Aboaf, J. A., and Pliskin, W. A., "Surface Oxidation of Silicon Nitride Films", J. Electrochem. Soc., 123, 560-565 (1976).**

ESCA is used to characterize Si_3N_4 surface oxidation. Oxidation at high temperature yields oxynitride films with gradients in composition.

343. **Restall, J. E., and Gostelow, C. R., "A Limited Assessment of Selected Low-Expansion Coefficient Ceramic Materials with Potential for High-Temperature Applications", Proc. Brit. Ceram. Soc., No. 22, 89-115 (1973).**

Of many materials examined for potential aircraft gas turbine engine components only Si_3N_4 and SiC exhibited the physical and mechanical properties above 1423 K to make them contenders for high temperature applications. An experimental glass-ceramic may be useful below that temperature.

344. **Rice, R. W., and McDonough, W. J., "Hot-Pressed Si_3N_4 With Zr Based Additives", J. Amer. Ceram. Soc., 58, 264 (1975).**

ZrO_2, ZrN, ZrC, and Zircon are effective aids in densification of Si_3N_4 by hot pressing to produce material with bend strength as high as 137 ksi.

345. **Rice, R. W., McDonough, W. J., and Becker, P. F., "Zirconia Additions to Hot Pressed Silicon Nitride", Rep. NRL Prog., 18-20 (December 1974).**

The addition of 3.0 w/o ZrO_2 - monoclinic or stabilized cubic form - improved the density (99% theoretical), creep, and oxidation resistance of hot-pressed Si_3N_4.

346. **Richerson, D. W., "Effect of Impurities on the High Temperature Properties of Hot-Pressed Silicon Nitride", Bull. Amer. Ceram. Soc., 52, 560-562, 569 (1973).**

Si_3N_4 specimens with controlled impurity levels were prepared by hot pressing and tested for flexural strength at 1375 C. Decreasing the metallic impurities increased flexural strength. High temperature properties of two specimens of different purities were compared.

347. **Robinson, A. L., "Ceramics: Brittle Materials for High Temperature Structures", Science, 187, 1185-1187 (March 28, 1975).**

Discusses advances in the use of refractory ceramic materials based on Si_3N_4 for high temperature applications.

348. **Rowcliffe, D. J., and Huber, P. A., "Hot Gas Stress Corrosion of Silicon Nitrides and Silicon Carbide", Proc. Brit. Ceram. Soc., No. 25, 239-252 (1975).**

Time-to-failure data are given for hot-pressed Si_3N_4 in combustion gases at 1173 and 1223 K. Na, Mg, and V additons to fuel don't affect failure times but failure in gas is more rapid than in air. Failure time is shorter at the higher temperature and room temperature fracture toughness can be increased by exposure to hot gas.

349. **Ruddlesden, S. N., and Popper, P., "On the Crystal Structures of the Nitrides of Silicon and Germanium", Acta Cryst., 11, 465-468 (1958).**

X-ray powder diffraction patterns of α- and β-Si_3N_4 and Ge_3N_4 were separated and indexed. The structures of the β-nitrides are of the phenacite type ($BeSiO_4$). The structure proposed for the α-nitrides is related to that of phenacite, one layer of phenacite type alternating with a similar but differently oriented layer in a hexagonal cell.

350. **Ryall, W. R., and Muan, A., "Silicon Oxynitride Stability", Science, 165, 1363-1364 (1969).**

Equilibrium measurements are reported on the approximate ratios of pressures of O to N, 10^{-15} at 1400-1500 C, required for the existence of Si_2N_2O under equilibrium conditions at elevated temperatures.

351. **Ryklis, E. A., Bolgar, A. S., and Fesenko, V. V., "Evaporation and Thermodynamic Properties of Silicon Nitride", Sov. Powder Met. Metal Ceram., No. 1, 73-76 (1969). Translation of Porosh. Met., No. 1, 92-96 (1969).**

Evaporation of Si_3N_4 was studied by the Langmuir and Knudsen methods in the temperature range 1688-1773 K. The compound dissociates into Si (solid or liquid depending on the temperature) and N. The rate of evaporation depends on the area of the effusion orifice. The equilibrium pressure of N above Si_3N_4, the evaporation coefficient, and the standard heat of formation were determined.

352. **Sage, A. M., and Histed, J. H., "Applications of Silicon Nitride", Powder Met., No. 8, 196-212 (1961).**

Summarizes known physical, mechanical and chemical properties of Si_3N_4 and compares them with properties of several ceramics and other materials in common use. It is shown how the combination of certain properties in Si_3N_4 make it an ideal material for six general types of applications.

353. **Saito, S., Somiya, S., and Kato, K., "Influence of Binders, Grain Sizes, Sintering Temperatures, and Atmospheres on Modulus of Rupture of Silicon Nitride Bodies", J. Jap. Soc. Powder Met., 13, 186-191 (1966). Translation of Funtai Oyobi Funmatsuyakin, 12, 187-198 (1965).**

Discussion of the effect of various binders on sintering of Si_3N_4.

354. **Samsonov, G. V., and Dobrovol'skii, A. G., "Some Aspects of the Technology for Producing Silicon Nitride Products", Refractories, No. 6, 369-372 (1966). Translation of Ogneupory, No. 6, 55-58 (1966).**

Comparison of two methods of preparing strong and dense Si_3N_4 articles. In one, blanks from powdered Si were formed and then nitrided producing only thin-walled articles. In the second, powders were formed and the blanks sintered producing thin- and thick-walled articles without inclusions of fused non-nitrided Si.

355. **Samsonov, G. V., Kazakov, V. K., Gorodetskii, S. S., and Kislyi, P. S., "Mechanical Properties of Al_2O_3-Si_3N_4 Oxide-Nitride Materials", Sov. Powder Met. Metal Ceramics, 13, 135-137 (1974). Translation of Porosh. Met., No. 2, 60-63 (1974).**

Mixed Al_2O_3-Si_3N_4 materials were made by cold pressing and sintering in a N atmosphere at various temperatures to 1650 C. Mullite formation claimed to activate sintering. Maximum observed bend strengths were ~6 kg/mm^2 (8.5 psi) and strengths decreased with increasing Al content.

356. **Samsonov, G. V., Kazakov, V. K., Gorodetskii, S. S., and Kislyi, P. S.,"Mechanical Properties of Magnesium Oxide-Silicon Nitride (Si_3N_4) System Materials", Izv. Akad. Nauk. SSSR Neorg. Mater., 9 (4), 8-10 (1973). (In Russian)**

The mechanical properties of materials in the MgO-Si_3N_4 system are dependent on composition, temperature, sintering time, and testing temperature. The optimum sintering temperature is 1600-1630 C. Strength is related to bulk density.

357. **Samsonov, G. V., Kazakov, V. K., Nazarchuk, T. N., Rogozinskaya, A. A., and Khorpyakov, O. T., "Sintering of High-Temperature Material Based on Silicon Nitride and Silicon Carbide", Soviet Powder Met. Metal Ceram., 10 (4), 271-275 (1971). Translation of Porosh. Met., 10 (4), 21-26 (1971).**

Study of the effects of temperature, composition of green powder, and gaseous medium on the structure and properties of materials of the Si_3N_4-SiC system. Products sintered under optimum conditions have improved mechanical properties due to the formation of a bond of Si_3N_4 that penetrates into the pores at high temperatures.

358. **Sata, T., and Urano, T., "Reactions Between Refractory Metals and Insulating Nitrides at High Temperatures", Yogyo Kyokai Shi, 78, 21-29 (1970). (In Japanese)**

Reaction of W and Ta with Bn, AlN, and Si_3N_4 were studied in Ar to 2100 C. W reacted with Si_3N_4 to form W_3Si_2. Ta formed TaN and $TaSi_2$.

359. **Schlichting, J., "Heisskoriosionverhalten von SiC und Si_3N_4 im Brennergas", Werkst. Korros., 26, 753-758 (1975).**

Si_3N_4 and SiC materials obtained by pyrolytic deposition are more resistant than sintered materials to corrosion in hot air and CH_4 combustion products containing various salts. Resistance is generally due to vitreous layer on ceramic surface.

360. **Scott, D., and Blackwell, J., "Hot Pressed Silicon Nitride as a Rolling Bearing Material - A Preliminary Assessment", Wear, 24, 61-67 (1973).**

A simple, accelerated service-simulation test was used to compare hot-pressed Si_3N_4 with other materials, under heavily loaded, lubricated, unlubricated, and elevated temperature rolling contact. The Si_3N_4 was the best commercially available wear resistant material tested under unlubricated ambient temperature conditions, but was not effective under heavily loaded lubricated conditions. Use of a solid lubricant at elevated temperature eliminated wear.

361. **Scott, D., Blackwell, J., and McCullagh, P. J.,"Silicon Nitride as a Rolling Bearing Material - A preliminary Assessment", Wear, 17, 73-82 (1971).**

Using a simple, accelerated service simulation test Si_3N_4 was compared with En 31 ball bearing steel, high speed tool steels and WC under conditions of heavily loaded, lubricated, unlubricated, and elevated temperature rolling contact. Low density, porous, heterogeneous reaction-bonded Si_3N_4 did not appear to be a suitable rolling material. Hot-pressed Si_3N_4 under lubricated test conditions was not as effective as En 31 and high speed tool steels and under unlubricated conditions was inferior to WC.

362. **Seaton, C. C., and Katz, R. N., "Acoustic Fatigue in Certain Ceramic Materials", J. Amer. Ceram. Soc., 56, 283 (1973).**

Acoustic fatigue occurred in thermally shocked TiB_2 and Al_2O_3, but not in hot-pressed Si_3N_4.

363. **Sharp, J. V., "Electron Microscopy of Oxidized Silicon Nitride", J. Mater. Sci., 8, 1755-1758 (1973).**

The internal structure of reaction-sintered Si_3N_4, after oxidation at 1000 C and 1400 C was examined by high voltage electron microscopy. A sheath region of amorphous SiO_2 around internal pores was formed after oxidation at both temperatures. The effects of oxidation on strength are discussed.

364. **Singh, R. N., and Tuohig, W. D., "Compatability of Si_3N_4 and $Si_3N_4 + Al_2O_3$ With Liquid Na and Li", J. Amer. Ceram. Soc., 58, 70-71 (1975).**

Na attacked grain boundaries at 550 C and Li caused extensive cracking at 400 C.

365. **Singhal, S. C., "Effect of Water Vapor on the Oxidation of Hot-Pressed Silicon Nitride and Silicon Carbide", J. Amer. Ceram. Soc., 59, 81-82 (1976).**

Oxidation rate of hot-pressed Si_3N_4 in O is slightly increased by addition of H_2O in temperature range 1200-1400 C. Nature of products and oxidation reactions are briefly discussed.

366. **Singhal, S. C., "Thermodynamics and Kinetics of Oxidation of Hot-Pressed Silicon Nitride", J. Mater. Sci., 11, 500-509 (1976).**

The "passive" oxidation behavior of Si_3N_4 hot pressed with 1 w/o MgO was studied at 1000-1400 C. The oxidation followed the classical parabolic behavior with an apparent activation energy of 375 $kJmol^{-1}$. The oxide film consists predominately of $MgSiO_3$, in which various impurity elements, Ca, Fe, Al, etc., concentrate. The rate controlling mechanism appears to be the outward diffusion of Mg ions and impurity cations from the grain boundary glass phase through the oxide film.

367. **Sleptsov, V. M., Shcherbina, O. D., and Trunov, G. V., "Removal of the Binder from Silicon Nitride", Sov. Powder Met. Metal Ceram., 14, 596-598 (1975). Translation of Porosh. Met., No. 7, 99-101 (1975).**

Binder was paraffin - 10% beeswax. Bend strength of slip-cast specimens was greater than that of pressed and sintered ones.

368. **Suzuki, H., "The Synthesis and Properties of Silicon Nitride", Bull. Tokyo Inst. of Tech., No. 54, 163-177 (1963). (In English)**

Effects of various catalyst additions on the nitriding of Si were studied experimentally. Selected additions were used to synthesize materials of compositions close to α-Si_3N_4 and β-Si_3N_4 respectively. Properties discussed include microstructure, lattice parameters, density, and thermal expansion.

369. **Swartz, J. C., "Atmosphere Effects on Wetting of Si_3N_4 by Liquid Si", J. Amer. Ceram. Soc., 59, 272-273 (1976).**

Wetting angle decreased with decreases in total pressure and N partial pressure, but wetting mechanisms are poorly understood.

370. **Taylor, D., "Reflected Light Microscopy of Silicon Nitride and Oxynitride", Trans. J. Brit. Ceram. Soc., 72, 319-321 (1973).**

Reflectivities of Si_3N_4 and Si_2ON_2 were 12.2% and 8.8% respectively. Differences in reflectivity between reaction-bonded α- and β-Si_3N_4 are so small that they could not be distinguished. Microhardness data show Si_3N_4 to be slightly harder than Si_2ON_2.

371. **Terwilliger, G. R., "Properties of Sintered Si_3N_4", J. Amer. Ceram. Soc., 57, 48-49 (1974).**

Si_3N_4 powder containing 5% MgO was sintered at 1650 C to 90% of theoretical density. High temperature mechanical properties, oxidation behavior, and room temperature dielectric properties are discussed.

372. **Terwilliger, G. R., and Lange, F. F., "Hot-Pressing Behavior of Si_3N_4", J. Amer. Ceram. Soc., 57, 25-29 (1974).**

The densification behavior of Si_3N_4 containing MgO was studied. Initially the MgO forms a liquid phase which wets and allows atomic transfer of Si_3N_4. Evidence of a second phase between grain boundaries was obtained. Transformation from α- to β-Si_3N_4 is unnecessary for densification.

373. **Terwilliger, G. R., and Lange, F. F., Pressureless Sintering of Si_3N_4", J. Mater. Sci., 10, 1169-1174 (1975).**

Liquid phase sintering and bulk decomposition are countervailing processes in the sintering of Si_3N_4 powder with 5 w/o MgO at 1500-1750 C. High densities can be achieved for long times at low temperatures or short times at high temperatures. Pore growth due to decomposition is said to limit shrinkage.

374. **Tetard, D., Lotholary, P., Goursat, P., and Billy, M., "Recherches sur les nitrides de silicium. IV: Cinétique d'oxidation du niture Si_3N_4 pulverulent", Rev. Int. Hautes Temp. Refract., 10, 153-159 (1973).**

Oxidation of Si_3N_4 powder was investigated at various O partial pressures at temperatures from 1050 to 1300 C. Oxidation rate depended on O pressure during induction period. Rate during latter stages was diffusion controlled. Activation energy (35 kcal $mole^{-1}$) agreed with that for diffusion of O in SiO_2.

375. **Thompson, D. S., and Pratt, P. L., "The Mechanical Properties of Reaction-Sintered Silicon Nitride", Proc. Brit. Ceram. Soc., No. 6, 37-47 (1966).**

Experimental values were obtained for mechanical properties of Si_3N_4 over a range of densities. Analyses of results for fracture strength in bending and Young's modulus show that reaction-sintered Si_3N_4 behaves as a normal porous ceramic body. All useful properties are attributed to the bulk material itself rather than to any effects of the reaction-sintered microstructure.

376. **Thorp, J. S., and Sharif, R. I., "Electrical Conductivity in Hot-Pressed Nitrogen Ceramics", J. Mater. Sci., 11, 1494-1500 (1976).**

A.C. and D.C. conductivities of Si_3N_4 and Si-Al-O-N compositions were measured between 400 and 1000 C. The materials were p-type below 900 C and n-type above 900 C. Electrical properties are consistent with presence of glassy phase.

377. **Torre, J. P., and Mocellin, A., "Some Effects of Al and O_2 on the Nitridation of Silicon Compacts", J. Mater. Sci., 11, 1725-1733 (1976).**

Highest final weight gains and densities were obtained when Si-Al compacts with homogeneous microstructure were nitrided in O-enriched atmospheres. X-ray diffraction analysis showed a β'-Si-Al-O-N solid solution. Obtaining this phase depends upon adjusting O content after N pressure of the reaction atmosphere has been set.

378. **Torti, M. L., "Silicon Nitride and Silicon Carbide - Properties and Shape Capability", Powder Met. Int., 6, 186-189 (1974).**

Describes hot pressing and sintering of Si_3N_4 and SiC and discusses advantages and limitations of each process.

379. **Torti, M. L., Alliegro, R. A., Richerson, D. W., Washburn, M. E., and Weaver, G. Q., "Silicon Nitride and Silicon Carbide for High-Temperature Engineering Applications", Proc. Brit. Ceram. Soc., No. 22, 129-146 (1973).**

Experimental results obtained with hot-pressed Si_3N_4 and SiC at temperatures up to 1500 C are presented. The variations in high temperature strength as a function of impurity content, strain rate, and grain size are discussed. Reaction-sintered Si_3N_4 and SiC are also discussed.

380. **Tressler, R. E., Meiser, M. D., and Yonushonis, T., "Molten Salt Corrosion of SiC and Si_3N_4 Ceramics", J. Amer. Ceram. Soc., 59, 278-279 (1976).**

Contaminent ion penetration can be substantial, and, in the case of Na, could affect mechanical properties.

381. **Tripp, W. C., and Graham, H. C., "Oxidation of Si_3N_4 in the Range 1300-1500°C", J. Amer. Ceram. Soc., 59, 399-403 (1976).**

Multiphase scales comprising mainly α-cristabolite and enstatite are oxidation products of commercial hot-pressed Si_3N_4. Large increase in rate at $>$1450 C is attributed to melting of scale. No O pressure dependence was found at 1400 C.

382. **Tsuge, A., Kudo, H., and Komeya, K., "Reaction of Si_3N_4 and Y_2O_3 in Hot-Pressing", J. Amer. Ceram. Soc., 57, 269-270 (1974).**

Si_3N_4 and Y_2O_3 powder mixtures were hot pressed at 1750, 1800, and 1850 C. Reaction products were identified and a proposed phase diagram is presented.

383. **Tsuge, A., Nishida, K., and Komatsu, M., "High-Temperature Strength of Hot-Pressed Si_3N_4 Containing Y_2O_3", J. Amer. Ceram. Soc., 58, 323-326 (1975).**

The effects of fabrication on the high temperature strength of hot-pressed Si_3N_4 containing 5 w/o Y_2O_3 were studied. Materials containing crystalline $Si_3N_4 \cdot Y_2O_3$ at grain boundaries had better high temperature strength than ones containing the same boundary composition in the glassy form.

384. **Turkdogan, E. T., Bills, P. M., and Tippet, V. A., "Silicon Nitrides: Some Physicochemical Properties", J. Appl. Chem., 8, 296-302 (May 1958).**

Si_3N_4 has been prepared by heating pure Si in purified N at 1450 C. X-ray studies showed the presence of two nitrides and a method was devised for separating them. These nitrides differ in crystal structure, but have the same composition corresponding to Si_3N_4. Chemical tests were performed on finely divided Si_3N_4 prepared at or above 1450 C. Various alloys, Si content varying, were nitrided under different conditions and the X-ray diffraction patterns of the nitrides extracted were found to agree with that of α-Si_3N_4.

385. **Ud Din, S., and Nicholson, P. S., "Creep Deformation of Reaction-Sintered Silicon Nitrides", J. Amer. Ceram. Soc., 58, 500-502 (1975).**

The steady-state creep behavior of reaction-bonded Si_3N_4 was examined in four-point bending with stresses ranging from 10,000 to 20,000 psi at 1200-1400 C. Creep rates were proportional to the 1.4 power of the stress. Microstructural examination indicated that the rate-controlling mechanism of creep is grain-boundary sliding.

386. **Ud Din, S., and Nicholson, P. S., "Creep of Hot-Pressed Silicon Nitride", J. Mater. Sci., 10, 1375-1380 (1975).**

High temperature creep tests (1200-1400 C) on hot-pressed Si_3N_4 showed the stress exponent of creep rate was $\sim$1.7 and the activation energy for creep was determined to be 140 kcal mol^{-1}. Creep is ascribed to grain-boundary sliding.

387. **Umebayashi, S., and Kobayashi, K., "β-Si_3N_4 Solid Solution Prepared from Volcanic Ash and Al Powder in N_2", J. Amer. Ceram. Soc., 58, 464 (1976).**

Evidence for solid solution of AlN in β-Si_3N_4. Product at highest heat treatment temperature (1400 C) comprised β-Si_3N_4 phase, AlN, and an unidentified phase.

388. **Umebayashi, S., and Kobayashi, K., "Refractory Material from Volcanic Ash and Aluminum Powder", Amer. Ceram. Soc. Bull., 54, 534 (1975).**

Refractory bodies were prepared from volcanic ash and 20-50 w/o powdered Al by sintering in a N atmosphere at 400 kg/cm^2 and 1400 C for 5 hours. α-Si_3N_4 whiskers were formed on the sintered bodies. Products included α-Al_2O_3 and β-Si_3N_4.

389. **Valentine, T. M., and Matkin, D. I., "Foamed Silicon Nitride", Proc. Brit. Ceram. Soc., No. 22, 281-289 (1973).**

Technique for production of foamed Si_3N_4, with controlled microstructure, using the rigid polyurethane foam route. Si_3N_4 foams with good compressive strength and porosities in the range of 90-60% have been fabricated. The fabrication, microstructure, and physical properties are presented.

390. **Valéry, N., "The Ceramic Engine Prepares for Takeoff", New Sci., 67 (967), 634-636 (1975).**

Ceramic components, as hot-pressed Si_3N_4, would allow the jet engine to operate at >300 degrees higher and thereby markedly reduce fuel consumption. These ceramics could even make the gas turbine a practical proposition for the motor car, allowing it to be produced and operated about as cheaply as a conventional petrol engine.

391. **Van Reuth, E. C., McLean, A. F., and Bratton, R. J., "Ceramic Gas Turbines for Improved Fuel Consumption", Naval Eng. J., 87, 109-114 (1975).**

Review of the status of Ford's ceramic gas turbine program. (See entry nos. 489-498). Properties, costs, and required design considerations for ceramics are highlighted.

392. **Vincenzini, P., Ceramurgia, 5 (4), 184-188 (1975). (See Entry No. 543).**

393. **Walton, J. D., Jr., "Reaction Sintered Silicon Nitride for High Temperature Radome Applications", Bull. Amer. Ceram. Soc., 53, 255-258 (1974).**

Si_3N_4 offers rain erosion resistance and thermal shock resistance in aerodynamic heating to velocities as high as Mach 7. Reaction-sintered Si_3N_4 is preferred for radomes and fabrication and dielectric data are given.

394. **Washburn, M. E., "Silicon Oxynitride Refractories", Bull. Amer. Ceram. Soc., 46, 667-671 (1967).**

Review of the discovery, preparation, and properties of Si_2ON_2. Specific heat, thermal conductivity, thermal expansion, modulus of rupture, modulus of elasticity, Knoop hardness, and electrical resistivity were measured. Oxidation studies showed oxidation resistance superior to SiC and Si_3N_4 at temperatures as high as 1750 C.

395. **Weston, R. J., and Carruthers, T. G., "Kinetics of Hot-Pressing of Alpha-Silicon Nitride Powder with Additives", Proc. Brit. Ceram. Soc., No. 22, 197-206 (1973).**

Si_3N_4 compacts of near theoretical density can be produced without significant conversion to β- form by hot pressing α-Si_3N_4 powders containing additives, chiefly 5 w/o MgO at 1500-1700 C and at pressures of 1 to 5 x 10^3 psi. MgO breaks down the amorphous SiO_2 layer which inhibits the deformation mechanism of the α-crystallites.

396. **Whalen, T. J., and Anderson, A. T., "Wetting of SiC, Si_3N_4 and Carbon by Si and Binary Si Alloys", J. Amer. Ceram. Soc., 58, 396-399 (1975).**

Wetting of Si_3N_4 by liquid Si and binary Si alloys containing Cu, Fe, and B were determined by the sessile drop method. All contact angles measured were <90 degrees. Hot-pressed Si_3N_4 is easily wet by Si.

397. **Wild, S., "A Novel Route for the Production of β' Sialon Powders", J. Mater. Sci., 11, 1972-1974 (1976).**

β'-sialon powders may be prepared in small amounts (0.2 g) by reaction of NH_3 or NH_3-H mixtures with kaolin.

398. **Wills, R. R., "Reaction of Si_3N_4 with Al_2O_3 and Y_2O_3", J. Amer. Ceram. Soc., 58, 335 (1975).**

Report of new phase $5Y_2O_3 \cdot Si_3N_4 \cdot Al_2O_3 \cdot Y_2O_3$ is an effective aid for sintering "sialon".

399 **Wills, R. R., "Silicon Yttrium Oxynitrides", J. Amer. Ceram. Soc., 57, 459 (1974).**

Role of Y_2O_3 in hot pressing of Si_3N_4 is to form low-melting $Si_3N_4 \cdot 3Y_2O_3$ which further reacts to form more refractory compound $Si_3N_4 \cdot Y_2O_3$. Diffraction data are given for both compounds.

400. **Wills, R. R., Cunningham, J. A., Wimmer, J. M., and Stewart, R. W., "Stability of the Silicon Yttrium Oxynitrides", J. Amer. Ceram. Soc., 59, 269-270 (1976).**

Oxidation at 1000 C of various Y-Si-O-N compositions produced weight gains and volume changes. Suggestions are given to minimize oxidation problems in Y_2O_3-based hot-pressed Si_3N_4.

401. **Wills, R. R., Holmquist, S., Wimmer, J. M., and Cunningham, J. A., "Phase Relationship in the System $Si_3N_4 \cdot Y_2O_3 \cdot SiO_2$", J. Mater. Sci., 11, 1305-1309 (1976).**

Examination of compositions in the system $Si_3N_4 \cdot Y_2O_3 \cdot SiO_2$ using sintered samples revealed the existance of two regions of melting and three $Si_3N_4 \cdot Y_2O_3$ phases. Two ternary phases and one binary phase were observed. It is suggested that Y_2O_3 promotes a liquid-phase sintering process which incorporates dissolution and precipitation of Si_3N_4 at the solid-liquid interface.

402. **Wills, R. R., Mendiratta, M. G., and Petrovic, J. J., "Controlled Surface - Flaw - Initiated Fracture in Reaction-Bonded Si_3N_4", J. Mater. Sci., 11, 1330-1334 (1976).**

Fracture was initiated at flaw, introduced by Knoop hardness indentation on bend specimen and K_{Ic} was calculated from stress to propagate flaw catastrophically. Vacuum annealing and heating above 1200 C reduced K_{Ic} 25%. This effect is ascribed to O and effects of oxidation are discussed.

403. **Wills, R. R., Stewart, R. W., Cunningham, J. A., and Wimmer, J. M., "The Silicon Lanthanide Oxynitrides", J. Mater. Sci., 11, 749-759 (1976).**

Silicon lanthanide oxynitrides are prepared by the reaction between Si_3N_4 and oxides of the lanthanide series. The oxides formed compounds of the type $Si_3N_4 \cdot R_2O_3$ and $R_4Si_2O_7N_2$ (R = lanthanide). Unit cells of these compounds are similar, and their structures are discussed in terms of those of known minerals.

404. **Wöhler, L., "Silicon and Nitrogen", Z. Elektrochem., 32, 420-423 (1926). (In German)**

Reviews previous work on the preparation and properties of Si_3N_4.

405. **Wruss, W., Kieffer, R., Gugel, E., and Willer, B., "Technological Investigations of the Silicon Nitride - Aluminum Oxide System", Sprechsael Keram. Glas. Baustoffe, 108, 378-383 (1975).**

Attempts to obtain a single-phase Si_3N_4 ceramic containing 5% MgO in the system $Si_3N_4 \cdot Al_2O_3$ were unsucessful. The physical and mechanical properties of the materials and phases of the $Si_3N_4 \cdot Al_2O_3$ system were studied.

406. **Yamamura, H., Kijima, K., Shirasaki, S., and Inomata, Y., "Mössbauer Effect of ^{57}Fe Doped Silicon Nitride", J. Mater. Sci., 11, 1754-1755 (1976).**

Suggests presence of N vacancies in Fe-doped Si_3N_4.

407. **Zabruskova, T. N., Guzman, I. Ya., and Dmitriev, I. A., "Stability of Silicon Oxynitride at High Temperatures", Refractories, 13, 118-121 (1972). Translation of Ogneupory, No. 2, 52-55 (1972).**

Si_2ON_2 is stable in an inert atmosphere at temperatures up to 1300 C but above this temperature (especially >1550 C), it rapidly volatilizes. Under these conditions the decomposition product is Si_3N_4. Decomposition in other atmospheres, particularly those containing O, is also discussed.

408. **Acquaviva, S. J., and Lum, P. T., "A Test for Fracture Toughness Determination of Ceramic Materials at Elevated Temperatures", Army Materials and Mechanics Research Center, Watertown, Massachusetts, Report No. AMMRC TN 75-5 (May 1975).**

Technique for obtaining high-temperature fracture toughness of ceramic materials, as Si_3N_4, is described. A free-falling ball was dropped onto a ceramic specimen and the fracture toughness was determined by taking the product of the weight of the ball and the height from which the ball dropped when fracture occurred. Results are given versus temperature for hot-pressed Si_3N_4.

409. **Akio, K., Yoshihro, O., Sanae, K., and Isao, M., "Formation of Finely Divided Silicon Nitride by Vapor Phase Reaction Between Silicon Tetrachloride and Ammonia", Army Foreign Science and Technology Center, Charlottesville, Virginia, Report No. FSTC-HT-23-1406-73 (May 1973). Translation of Yogyo Kyokai Shi, 80 (3), 28-34 (1972). (AD-B000 154L)**

Si_3N_4 was synthesized at 1050-1500 C. The structure of the products was studied by X-ray diffraction, IR atomic spectroscopy, chemical analysis, and electron microscopy.

410. **Alliegro, R. A., and Coes, S. H., "Reaction Bonded Silicon Carbide and Silicon Nitride for Gas Turbine Applications", ASME Publication 72-GT-20 (January 1972).**

Recrystallized SiC made by a casting process and reaction-bonded Si_3N_4 shaped by a simple machining process before firing, offer not only high-temperature materials capable of living in the gas turbine environment, but also at an intricacy of shape consistent with combustor, shroud, and associated high-temperature component needs. The low expansion coefficient, thermal shock resistance, and 2900 F capability make Si_3N_4 a material of real merit. Properties, potential applications, and design capabilities are discussed.

411. **Andersson, C. A., Lange, F. F., and Iskoe, J. L., "Effect of the MgO/SiO_2 Ratio on Strength of Hot-Pressed Si_3N_4: Interrelation Between Creep and Slow Crack Growth, Crack Extension and Arrest: Theory and Experiments for Contact Stress Fields", Westinghouse Electric Corporation, Pittsburgh, Pennsylvania, Office of Naval Research Contract Report (October 1975). (AD-A016 803)**

Significant increases in strength at 1400 C were observed as the MgO/SiO_2 ratio was increased to 3:4. Observations are discussed with regard to possible changes in chemistry of grain boundary phase.

412. **Bart, R. K., Hauck, E. W., and Torti, M. L., "Experience in the Manufacture of Gas Turbine Vanes of Hot Pressed Silicon Nitride and Silicon Carbide", ASME Publication 75-GT-99 (December 1974).**

A review of materials development programs showing that hot-pressed Si_3N_4 and SiC are consistent engineering materials for gas turbine vanes. General machining parameters, including diamond wheel specifications are discussed.

413. **Baumgartner, H. R., and Cowley, P. E., "Finishing Techniques for Silicon Nitride Bearings", Norton Company, Worcester, Massachusetts, Army Materials and Mechanics Research Center, Contract Report No. AMMRC CTR 76-5 (March 1976). (AD-025 350)**

After 27 different surface finishing procedures, strength, surface finish, and rolling contact fatigue life were determined for two grades of hot-pressed Si_3N_4. Rolling contact fatigue lives of Si_3N_4 with selected smoother finishes tested at 800 ksi Hertz stress were an order of magnitude longer than those obtained on the M50 bearing steel controls and more than twice as long as the best results previously obtained on Si_3N_4.

414. **Baumgartner, H. R., and Cowley, P. E., "Silicon Nitride in Rolling Contact Bearings", Norton Company, Worcester, Massachusetts, Naval Air Systems Command Contract Report (August 1975). (AD-A015 990)**

Six hot-pressed Si_3N_4 materials of varying composition were prepared, characterized, and evaluated in rolling contact fatigue (RCF). All equaled or exceeded the fatigue life of M50 steel at 325 lb load. A stress corrosion mechanism is used to explain the time-dependent fatigue behavior and life differences are attributed to differences in slow crack growth rates. Ten precision bearings containing Si_3N_4 rollers and steel races were designed, fabricated, and tested.

415. **Baumgartner, H. R., Sundberg, D. V., and Wheildon, W. M., "Silicon Nitride in Rolling Contact Bearings", Final Report, 3 January-30 October 1973, Norton Company, Worcester, Massachusetts, Naval Air Systems Command Contract Report (October 1973). (AD 771 393)**

Hot-pressed Si_3N_4 evaluated as bearing material. Reports rolling contact fatigue tests of Si_3N_4 rods, and design, fabrication, and testing of full-scale roller bearings.

416. **Brennan, J. J., "Development of Fiber-Reinforced Ceramic-Matrix Composites", United Aircraft Corporation, East Hartford, Connecticut, Naval Air Development Center Contract Report No. UARL-N911647-4 (April 1974). (AD 778 651)**

The incorporation of Ta wire increased the Charpy impact strength of hot-pressed Si_3N_4 from 0.5 to 14.8 ft/lbs. Specimens containing 50-mil wire retained impact strength to 1300 C. Data are also given on ballistic-impact, thermal-shock and thermal-aging resistance.

417. **Brennan, J. J., "Development of Fiber Reinforced Ceramic Matrix Composites", United Aircraft Research Laboratories, East Hartford, Connecticut, Naval Air Development Center Contract Report No. UARL-R911848-4 (February 1975). (AD-A009 360)**

Hot-pressed Si_3N_4 matrix composites containing 5-15 w/o Y_2O_3 and reinforced with Ta wire exhibited excellent thermal fatigue and thermal shock properties, as well as impact resistance. Ta-reinforced material was as good as or better than the unreinforced material in creep at 1300 C. Component vanes and wedge shapes of both Si_3N_4 and the Ta-reinforced materials have been formed with minimal finish grinding using the "pseudo-isostatic" hot pressing technique.

418. **Brennan, J. J., "Investigate Fiber Reinforced Si_3N_4", United Technologies Research Center, East Hartford, Connecticut, Naval Air Development Center Contract Report No. R76-912081-4 (March 1976). (AD-A025 901)**

Ta wire reinforcement in hot-pressed Si_3N_4-15 w/o Y_2O_3. Room- and high-temperature properties of matrix and reinforced materials were superior to those of other materials tested.

419. **Brennan, J. J., and DeCrescente, M. A., "Fiber Reinforced Ceramic Matrix Composites", United Aircraft Research Laboratories, East Hartford, Connecticut, Naval Air System Command Contract Report No. M911294-4 (January 1973). (AD 757 063)**

Charpy impact strength of Si_3N_4 reinforced with W was increased at elevated temperature but not at room temperature. With Ta wire reinforcements, Charpy impact strength increased at room temperature and the mode of failure was affected so that interfacial splitting along with ductile fiber elongation occurred, resulting in very small fragments of matrix breaking off upon impact.

420. **Burns, F. C., Priest, H. F., and Priest, G. L., "Characterization of Silicon Nitride Using 14MeV Neutrons", Army Materials and Mechanics Research Center, Watertown, Massachusetts, Report No. AMMRC MS 75-6 (September 1975). (AD-A033 690)**

Technique is described and results are presented on determination by neutron activation analysis of O in hot-pressed and reaction-sintered Si_3N_4.

421. **Campo, J., "Utilization of the Bend Test for Determining Tensile Properties of a Brittle Material", Army Materials and Mechanics Research Center, Watertown, Massachusetts, Report No. AMMRC TR 75-17 (August 1975). (AD-A016 129)**

Bend and tension tests were performed at room temperature on a commercial Si_3N_4 material. Using the two-parameter Weibull analyses for a material governed by volumetric flaw distribution, tensile properties of the specimen were determined and compared. Results indicated that the bend test tends to predict fracture stresses ~8% higher than those obtained in actual tension tests.

422. **Cannon, R. M., Jr., and Hill, R. J., "High Temperature Compounds for Turbine Vanes", Avco Corporation, Systems Division, Lowell, Massachusetts, National Aeronautics and Space Administration Contract Report No. NASA CR-72794 (August 1970). (N71-15082)**

Fibrous materials such as SiC whiskers were added to SiC and Si_3N_4 and the resulting composites were consolidated by hot pressing. Addition of the SiC whiskers increases the impact strength of the SiC from 0.55 in/lbs (0.062 J) to 1.6 in/lbs (0.18 J) at room temperature and from 0.64 in/lbs (0.07 J) to 1.35 in/lbs (0.153 J) at 2400 F and the Si_3N_4 from 1.05 in/lbs (0.119 J) to 1.33 in/lbs (0.15 J) at room temperature and from 1.31 in/lbs (0.15 J) to 1.68 in/lbs (0.19 J) at 2400 F. Si_3N_4 has a higher impact strength than SiC. The thermal stability and shock resistance of the composites were determined under simulated gas turbine stator vane environments at 2400 F. The presence of whiskers did not seriously affect either characteristic.

423. **Carr, E. M., and Bartlett, R. W., "Evaluation of Duplex Whisker-Crystalline Silicon Nitride Structures", Stanford Research Institute, Menlo Park, California, Air Force Materials Laboratory Contract Report No. AFML-TR-68-197 (August 1968). (AD 840 593)**

Study of the processing characteristics and physical properties of Si_3N_4 ceramic bodies with duplex microstructure formed by "in situ" vapor reaction between Si powder compacts and N.

424. **Caws, R. B., Graham, R. P., and Stoddart, D. E., "Silicon Nitride Materials for Gas Turbine Components", ASME Publication 73-GT-47 (1973).**

Discusses design, processing, and testing of Si_3N_4 components for gas turbines.

425. **"Ceramic Materials and Components for Small Automotive Gas Turbine Engine", Report on Technology Assessment and Implementation Plan FY 76-81, Army Materials and Mechanics Research Center, Watertown, Massachusetts (April 1975). (AD-A025 472)**

The beneficial impact in future energy demands, multiple fuel potential, and lessened dependence on foreign materials are sufficient motivation to initiate the recommended programs.

426. **Chin, J., and Elsner, N. B., "Preparation of Silicon-Aluminum-Nitrogen Compounds by Reactive Ion Plating", General Atomic Company, San Diego, California, U. S. Energy Research and Development Administration Contract Report No. GA-A-13432 (April 1975).**

(Si, Al)N Alloys were deposited by reactive ion plating from Si and Al evaporation and NH_3 or NH_3 + 1% SiH_4 gas mixtures. Deposits had large columnar grains composed of smaller grains. At temperatures from 100-300 C there were no observable changes in morphology. Adhesion of deposits to a variety of surfaces was good.

427. **Congleton, J., and Denton, B. K., "Dynamic Fracture Toughness Measurement", University of Newcastle-Upon-Tyne (England), Department of Army Grant No. DA-ERO-124-74-G0053 (July 1975). (AD-A016 933)**

An improved crack velocity monitoring procedure able to cope with irregular crack initiation and crack acceleration in ceramics was developed and used to obtain K_{id} measurements for Si_3N_4 and other ceramic materials.

428. **Crandall, W. B., Hed, A. Z., and Shipley, L. E., "Preparation and Evaluation of Si-Al-O-N", IIT Research Institute, Chicago, Illinois, Aeronautical Research Laboratory Contract Report No. ARL-74-0099 (June 1973).(AD-A021 997)**

Specimens were prepared of Si-Al-O-N compositions to permit evaluation of chemical, physical, and mechanical properties. Several different processing techniques were used on various precursor materials. Moduli of rupture and elasticity measurements were made and strength values were lower than expected from literature data.

429. **Dalal, H., Chiu, Y. P., and McCool, J. I., "Surface Interactions and Lubrication Response of Silicon Nitride Bearing Elements", SKF Industries, King of Prussia, Pennsylvania, Naval Air Systems Command Contract Report No. AL74P009 (February 1974). (AD 777 087)**

Basic studies on the suitability of Si_3N_4 binders as a rolling bearing material with emphasis on interactive behavior with lubricating fluids are reported. The wetabilities of six lubricants on a Si_3N_4 surface were measured. Lubricant film thickness and traction force were measured with an optical elastohydrodynamic apparatus.

430. **Dalal, H. M., Chiu, Y. P., and Rabinowicz, E., "Evaluation of Hot Pressed Silicon Nitride as a Rolling Bearing Material", ASLE Preprint 74LC-5A-4, 1974.**

Wettability, lubricant film thickness, rolling/sliding traction coefficients, sliding friction coefficients, abrasive wear coefficient, and rolling contact fatigue of Si_3N_4 suggest that it possesses satisfactory ability to be lubricated by conventional lubricants, as well as good mechanical strength and fatigue resistance properties.

431. **Dalal, H., Hahn, D., and Ninos, N., "Surface Endurance and Lubrication of Silicon Nitride Ball Bearings", SKF Industries, Inc., King of Prussia, Pennsylvania, Naval Air Systems Command Contract Report No. SKF-AL75T030 (December 1975). (AD-A022 157)**

Life of M50 steel bearings with Si_3N_4 balls is controlled by life of currently available Si_3N_4 balls. Bearing behavior is illustrated and described.

432. **Dalal, H., Hahn, D., and Rhoads, W. L., "Effect of Surface and Mechanical Properties on Silicon Nitride Bearing Element Performance", SKF Industries, Inc., King of Prussia, Pennsylvania, Naval Air Systems Command Contract Report No. SKF-AL75T002 (February 1975). (AD-A006 917)**

Importance of understanding surface damage effects is emphasized. Rolling contact fatigue tests were done between Si_3N_4 and steel. Variables included lubricant viscosity, surface finish, type of contact (line or point), and hardness of steel rollers. Concludes that Si_3N_4 rolling elements can improve fatigue life of very high-speed bearings.

433. **Dapkunas, S. J., "Ceramics for Gas Turbine Applications (A State-of-the-Art Survey)", Naval Ship Research and Development Center, Annapolis, Maryland, Research Report No. NSRDC-4199 (May 1974). (AD 780 440)**

Mechanical properties, oxidation, and hot corrosion of Si_3N_4 and SiC are presented for comparison with those of superalloys. The hot-pressed ceramics are shown to have superior strength and environmental resistance but are lacking in impact strength. Reaction-sintered Si_3N_4 is shown to be a low-cost, low-strength material.

434. **Davidge, R. W., "The Mechanical Properties and Design Data for Engineering Ceramics", Mechanical Property Testing of High Temperature Materials, Advisory Group for Aerospace Research and Development, Paris, France, Report No. AGARD-R- 634 (December 1975). (AD-A019 758)**

Review of the mechanical properties and design data of ceramic components, including reaction-sintered and hot-pressed Si_3N_4 and SiC with emphasis on the materials science considerations. General recommendations for future are made.

435. **Derkacs, T., Matay, I. M., and Brentnall, W. D., "Nondestructive Evaluation of Ceramics", TRW, Incorporated, Cleveland, Ohio, Naval Air Systems Command Contract Report No. TRW-ER-7798-F (May 1976). (AD-A027 357)**

An ultrasonic nondestructive evaluation (UNDE) technique was developed to detect small defects in gas-turbine quality SiC and Si_3N_4. Conventional mechanical tests were also performed to verify defect sizes and to correlate material strength with UNDE results.

436. **Engel, W., Porz, F., and Thuemmler, F., "Measurement of Internal Oxidation of Reaction-Bonded Silicon Nitride During Creep", Scientific Translation Service, Santa Barbara, California, National Aeronautics and Space Administration Contract Report No. NASA-TT-F-17134 (August 1976). Translation of Ber. Dtsch. Keram. Ges., 52 (1975), pp 296-299. (N76-28368)**

Concentrations of Si_2ON_2 cristabolite, and β-Si_3N_4 were determined over cross sections of reaction-bonded (2.20 g/cc) Si_3N_4 specimens creep tested at different rates under oxidizing conditions. Internal oxidation degrades creep resistance.

437. **"Engineering Property Data on Selected Ceramics. Volume I, Nitrides", Metals and Ceramics Information Center, Battelle's Columbus Laboratories, Columbus, Ohio, Report No. MCIC-HB-07-Vol. I (March 1976), section 5.3.3. (AD-A023 773)**

Property data including physical, thermal, mechanical, and other properties for hot-pressed and reaction-sintered Si_3N_4, silicon oxynitrides and sialons are presented in detail.

438. **Ferraro, T. A., Jr., and Strauss, B. H., "Emission Spectrographic Determination of Metallic Impurities in Silicon Nitride by a Solution Method", Army Materials and Mechanics Research Center, Watertown, Massachusetts, Research Report No. AMMRC PTR 73-5 (April 1973). (AD 761 104)**

Si_3N_4 samples were dissolved in teflon-lined acid digestion bombs using a mixture of HF and HNO_3. The Si was removed as the volatile fluoride and the samples were analyzed by a solution-spectrographic method. Results and standard deviations for Al, Fe, Ti, Cr, Mn, Mg, and Ca are reported and compared with values obtained by spectrophotometric methods.

439. **Fessler, H., Sivill, A. D., and Stanley, P., "Thermomechanical Stress Analysis of Silicon Nitride Components", Defence Research Information Center, Orpington, England, Report No. DRIC-BR-46801 (June 1975). (AD-B007 563L)**

Design procedure based on Weibull statistics.

440. **Fisher, E. A., and McLean, A. F., "Current Status of High Temperature Ceramic Gas Turbine Research and Development", SAE Publication 741047 (1974). (See Entry Nos. 489-498)**

Review of Ford's ceramic gas turbine program.

441. **"Fracture of Ceramics. A Bibliography with Abstracts", National Technical Information Service, Springfield, Virginia, Report No. NTIS /PS-76/0198 (1976).**

Citations of research (1964-1975) on ceramic fracture in relation to fabrication, microstructures, mechanical properties, and composition. Reports include ceramic use in rocket components, gas turbines, nuclear reactors, and structural parts. Pertinent reports are annotated in this bibliography with each entry under the name of the specific author.

442. **Gazza, G. E., "Silicon Nitride/Yttria: A Potential Gas Turbine Material", Army Materials and Mechanics Research Center, Watertown, Massachusetts, paper presented at the Army Science Conference (1976). (AD-A025 998)**

Y_2O_3 is an effective densification aid to Si_3N_4. Significant increases in strength and stress-rupture properties have been demonstrated for the Si_3N_4-Y_2O_3 system at temperatures of 2400-2500 F, as compared to the Si_3N_4-MgO system. Additional work is needed to assess the performance of the Y_2O_3 material in the gas turbine environment.

443. **Gazzara, C. P., and Messier, D. R., "Quantitative Determination of Phase Content of Silicon Nitride by X-Ray Diffraction Analysis", Army Materials and Mechanics Research Center, Watertown, Massachusetts, Technical Report No. AMMRC TR 75-4 (February 1975). (AD-A008 986)**

A method was developed for the rapid determination by X-ray diffraction analysis of weight fractions of phases in mixtures of α-Si_3N_4, β-Si_3N_4, and Si. The heights of several peaks of each phase were averaged to minimize preferred orientation effects. Extinction effects were negligible except for the Si phase. The measured composition of a known standard was within 1-2% of its actual composition.

444. **Gazzara, C. P., and Reed, D., "A Computed X-Ray Diffraction Powder Pattern for Alpha and Beta Silicon Nitride", Army Materials and Mechanics Research Center, Watertown, Massachusetts, Report No. AMMRC TN 75-4 (April 1975).**

The CuK_α and CuK_β X-ray diffracted integrated intensities from α- and β-Si_3N_4 powders were computed using the known atomic position parameters. Also listed are 2θ, d-spacing, structure factor and multiplicity values. The computed intensities agree with those determined experimentally.

445. **Gielisse, P., Kim, T. J., Choudry, A., Short, J. F., and Turker, E. J., "Force and Wear Analysis in Ceramic Processing ", University of Rhode Island, Kingston, Naval Air Systems Command Contract Report No. URI-9804-4047 (November 1972). (AD 762 522)**

Grinding forces were determined for four aluminas and hot-pressed Si_3N_4. Relative wear rates were determined for all materials and conditions. Wear is related linearly to Young's modulus. Ceramic grinding temperature is 1477 C for Si_3N_4.

446. **Gielisse, P. J., Wilson, M. P., Borase, V. N., Heung, L. K., and Kiehle, A. J., "Ceramic Materials for High Temperature Gas Bearings", Rhode Island University, Kingston, Office of Naval Research Contract Report No. URI-9804-4046 (September 1972). (AD 753 858)**

Hot-pressed Si_3N_4 was evaluated for application as a high-temperature gas bearing material. The results of a start-stop and a continuous-run thrust washer test in terms of coefficient of friction and mode of wear are reported. Properly prepared surfaces should give a coefficient of friction of 0.1. The extent and type of wear appear to depend on the congruency of the mating surfaces. A compilation of the properties of Si_3N_4 is provided in the Appendix.

447. **Godfrey, D. J., "Silicon Nitride Ceramics for Engineering Applications", SAE Publication 740238 (1974).**

A review of the variety of Si_3N_4 and SiC materials and their performance and economics.

448. **Greskovich, C. D., Rosolowski, J. H., and Prochazka, S., "Ceramic Sintering", General Electric Corporate Research and Development, Schenectady, New York, Office of Naval Research Contract Report No. SRD-75-084 (July 1975). (AD-A014 480)**

Measurements of the rate of oxidation and of creep in air of CVD Si_3N_4 at ~1500 C are reported. Attempts to prepare pure, dense Si_3N_4 bodies by hot-pressing powder at ultra-high pressures were partially successful. Work on the sintering of covalently bonded solids, β-SiC, Si, α-Si_3N_4, AlN, is presented.

449. **Griffin, I. M., and Mead, A. P., "Determination of Oxygen in Silicon Nitride by Inert Gas Fusion", Atomic Energy Research Establishment, Harwell, England, Report No. AERE-R-5878 (August 1968). (N69-23939)**

In the method described, the sample, encapsulated in a platinum tube, is reacted with C, first at 1300 and then at 2100 C, the CO formed at each temperature being removed in a stream of high-purity He. After oxidation of the CO with Cu_2O the CO_2 is frozen out in a multiloop trap and finally measured in an open-well capillary manometer. The two heating temperatures distinguish between "free" or adsorbed O and combined O.

450. **Gruver, R. M., and Kirchner, H. P., "Effect of Leached Surface Layers on Impact Damage and Remaining Strength of Si_3N_4", Localized Impact Damages in Ceramics, Ceramic Finishing Company, State College, Pennsylvania, Office of Naval Research Contract Report No. TR-3 (January 1976). (AD-A021 496)**

Hot-pressed Si_3N_4 was leached with HF and subjected to impact at low velocities by a WC sphere. The remaining strength of the leached specimens after impact was substantially greater than those that were not leached. The leached layers prevented formation of Hertz cracks in the underlying material.

451. **Gruver, R. M., Sotter, W. A., and Kirchner, H. P., "Fractography of Ceramics", Summary Report, 22 February 1973-22 November 1974, Ceramic Finishing Company, State College, Pennsylvania, Naval Air Systems Command Contract Report (November 1974). (AD-A003 911)**

Al_2O_3, Si_3N_4, and SiC specimens were fractured at various loading rates and temperatures and the fracture surfaces studied by optical and scanning electron microscopy. Fracture origins were located and the flaws at the fracture origins identified, characterized, and classified. Applications of results to ceramic processing, designing with brittle materials, and theory of fracture are discussed.

452. **Gulden, M. E., and Metcalfe, A. G., "Static Fatigue of Ceramic Materials", Interim Technical Report, 1 April 1973-31 January 1974, Solar Division of International Harvester Company, San Diego, California, Office of Naval Research Contract Report No. RDR-1778-1 (February 1974). (AD 774 934)**

Time-dependent failure of hot-pressed and reaction-sintered Si_3N_4 in the temperature range from 0-900 C was studied. The tests were carried out in air saturated at room temperature with H_2O in order to identify the temperature range where static fatigue phenomena are important and also to identify the moisture-related stress corrosion process. Reaction-sintered Si_3N_4 did not exhibit strain rate dependence of strength in the temperature range tested. Delayed failure of hot-pressed Si_3N_4 is moisture related.

453. **Gulden, M. E., and Metcalfe, A. G., "Static Fatigue of Ceramic Materials", Second Interim Technical Report, 30 January 1974-30 June 1974, Solar Division of International Harvester Company, San Diego, California, Office of Naval Research Contract Report No. RDR-1778-2 (July 1974). (AD 786 231)**

Time-dependent failure of commercial Si_3N_4 materials in the temperature range ambient to 900 C was studied using variable strain rate and static load tests in four-point bending. Room-temperature strength decrease for hot-pressed Si_3N_4 was found to be moisture dependent and more marked in the presence of acids. Reaction-sintered Si_3N_4 showed static fatigue, but its strength was independent of strain rate. Proposed theory attributes static fatigue to ion exchange in glass grain-boundary phase.

454. **Guzman, I. Ya., and Tumakova, Ye. I., "The Question of Producing Articles from Silicon Nitride", Foreign Technology Division, Wright-Patterson Air Force Base, Ohio, Report No. FTD-MT-24-301-69 (November 1969), pp 1-7. Translation of Tr. Khim. Teknal. Inst., No. 50 (1966), pp 201-204.**

Si_3N_4 was obtained by firing pressed specimens of Si and SiC in a N atmosphere. Data presented include the dependence of weight gain, density, and compressive strength on the SiC content of the material.

455. **Harris, J. N., "Investigation of Reaction Sintered Silicon Nitride as a Radome Material", Final Report,1 December 1973-28 February 1975, Georgia Institute of Technology, Atlanta, Naval Air Systems Command Contract Report No. GIT-A-1585-F (March 1975). (AD-A012 439)**

Study of the formation of reaction-bonded Si_3N_4 radomes from slip-cast Si. Costs are compared with SiO_2 and fabrication procedures are described. Also included are transmission and pattern degradation results on small radomes. Densities ranged from 2.0-2.6 g/cm^3, but acceptable electrical properties are difficult to obtain at higher densities.

456. **Harris, J. N., "Investigation of Reaction Sintered Silicon Nitride as a Radome Material", Final Report, 1 March 1975-31 August 1975, Georgia Institute of Technology, Atlanta, Naval Air Systems Command Contract Report No. GIT-A-1724-F (October 1975). (AD-A019 133)**

Eleven reaction-sintered Si_3N_4 radomes were prepared by slip casting Si blanks and reaction sintering in N. Items investigated were repeatability of electrical transmission characteristics, methods of sealing pores, attachment systems, and preparation of a radome for rain erosion sled testing.

457. **Harris, J. N., Arrietta, R. A., and Byers, S. A., "An Investigation of Reaction Sintered Silicon Nitride as a Radome Material", Final Report 1 December 1972-30 November 1973, Georgia Institute of Technology, Atlanta, Naval Air Systems Command Contract Report (December 1973). (AD 777 064)**

Reaction-bonded Si_3N_4, containing up to 1% Fe and fabricated by injection molding was studied as a candidate radome material. Fabrication equipment and techniques and test techniques for thermal, mechanical, and electrical evaluation are described. Results suggest a direct relationship between final sintered density and dielectric properties.

458. **Hayes, C. W., "Turbine Vane Ceramic Endwall Program", Pratt and Whitney Aircraft, East Hartford, Connecticut, Air Force Aero-Propulsion Laboratory Contract Report No. AFAPL-TR-74-103 (August 1974). (AD-A009 168)**

Turbine vane platforms were fabricated from hot-pressed Si_3N_4 and tested at elevated temperature in a cascade of transpiration-cooled turbine vanes representative of advanced engine concepts. There was no damage after steady-state endurance testing for 10 hours at >2000 C.

459. **Hayman, C., Stuart, M. C., and Bines, E. B., "Thermodynamic Investigation of Compounds in Rocket Propulsion", Final Scientific Report 1 January 1972-30 June 1974, Fulmer Research Institute Ltd., Stoke Pages (England), Air Force Office of Scientific Research Contract Report No. AFOSR-TR-74-1798 (October 1974). (AD-A001 845)**

Preliminary estimates of enthalpies of formation of α- and β-Si_3N_4 by combustion in fluorine were determined from calorimetric measurements.

460. **Iskoe, J. L., and Lange, F. F., "Development of Microstructure, Strength and Fracture Toughness of Hot Pressed Si_3N_4", Westinghouse Research and Development Center, Pittsburgh, Pennsylvania, Office of Naval Research Contract Report No. TR-7 (April 1976). (AD-A024 268)**

The structural development of Si_3N_4, hot pressed from a high α-phase powder with MgO additions, was observed using scanning electron microscopy. The extent of the concurrent densification processes, $\alpha \rightarrow \beta$ transformation, and development of mechanical properties was determined as a function of time, temperature, and MgO content. Full densification occurred prior to the completion of the $\alpha \rightarrow \beta$ transformation. Maximum strength was independent of time and temperature once full density was achieved. Relationship between α/β transformation and fibrous microstructure is discussed.

461. **Iskoe, J. L., and Lange, F. F., "Effect of Selected Impurities on the High Temperature Mechanical Properties of Hot-Pressed Silicon Nitride", Westinghouse Research Laboratories, Pittsburgh, Pennsylvania, Office of Naval Research Contract Report No. 74-9D4-KERAM-R2 (April 1974). (AD 783 506)**

Selected impurities as Al_2O_3, CaO, Fe_2O_3, Li_2CO_3, and Na_2CO_3 were added to relatively pure β-Si_3N_4 powders and subsequently hot pressed to full density using MgO 5 w/o as the pressing additive. None of the impurities affected room temperature strength and only CaO affected high-temperature strength. High-purity, high-α-Si_3N_4 powder was produced, but no details are given.

462. **Iskoe, J. L., Lange, F. F., and Diaz, E. S., "Effect of Selected Impurities on the High Temperature Mechanical Properties of Hot-Pressed Silicon Nitride", Westinghouse Electric Corporation, Pittsburgh, Pennsylvania, Office of Naval Research Contract Report No. 74-9D4-POWDR-R2 (October 1974). (AD-A002 251)**

Reduction in high-temperature strength and creep resistance of commercial hot-pressed Si_3N_4 is shown to be associated with impurities. Selected impurities including oxides and carbonates were added to α- and β-Si_3N_4 starting powders that were hot pressed to full density using 5 w/o MgO as the pressing additive. The Si_3N_4 hot pressed from the α-powder exhibited higher strengths at both 25 and 1400 C. Room-temperature mechanical properties were uneffected by the impurity additions.

463. **Jacobson, L. A., and Drewry, J. E., "Preliminary Study on the Use of Ceramic Nozzle Arrays in Gas Dynamic Lasers", Aerospace Research Laboratories, Wright-Patterson AFB, Ohio, Report No. ARL-75-0100 (April 1975). (AD-A010 618)**

A model gas dynamic laser (GDL) nozzle array was fabricated from hot-pressed Si_3N_4 components and tested under thermal cycling air flow conditions to 1150 K. Excellent dimensional stability was shown by the center nozzle of the three-nozzle assembly and examination revealed no degradation of the materials.

464. **Johnson, R. C., Warwick, W. H., and Shell, H. R., "Synthesis and Some Properties of Fibrous Silicon Nitride", U. S. Bureau of Mines, Washington, D. C., Report No. BM-RI-6467 (1964).**

α-Si_3N_4 fibers were successfully grown in graphite crucibles by a new method using silicates and Si as sources of Si and using C, Al, and Si as reducing agents. A build-up of coatings on the solid raw material particles hindered the evolution of Si or SiO vapor and thereby slowed down further formation of Si_3N_4 fibers.

465. **Kamiya, N., Oyama, Y., and Kamigaito, O., "Silicon Nitride Solid Solution in the Ternary System Si_3N_4-AlN-SiO_2", Scientific Translation Service, Santa Barbara, California, National Aeronautics and Space Administration Contract Report No. NASA-TT-F-16904 (November 1975). Translation of Yogyo Kyokai Shi, 83 (1975), pp 553-557. (N76-18235)**

Expected compounds were not found. Suggests addition of AlN to Si_3N_4 would eliminate glassy phase which decreases high-temperature strength.

466. **Kirchner, H. P., "Strengthening of Oxidation Resistant Materials for Gas Turbine Applications", Ceramic Finishing Company, State College, Pennsylvania, National Aeronautics and Space Administration Contract Report No. NASA-CR-134661 (June 1974). (N75-10092)**

Compressive surface layers were formed on Si_3N_4 by quenching and/or carburizing. In some cases impact resistance and/or flexural strength were increased.

467. **Kirchner, H. P., Gruver, R. M., and Miller, C. S., "Localized Impact Damage in Hot Pressed Si_3N_4 and SiC", Localized Impact Damage in Ceramics, Ceramic Finishing Company, State College, Pennsylvania, Office of Naval Research Contract Report No. TR-3 (January 1976). (AD-A021 496)**

The strength degradation of hot-pressed Si_3N_4 and SiC due to impacts by spheres at low velocities was determined. Results showed that the impact force necessary to form Hertz cracks in Si_3N_4 was ~4 times that for SiC. The cracks were characterized and the dimensions compared with calculated values.

468. **Kirchner, H. P., and Seretsky, J., "Improving Impact Resistance of Ceramic Materials by Energy Absorbing Surface Layers", Ceramic Finishing Company, State College, Pennsylvania, National Aeronautics and Space Administration Contract Report No. NASA-CR-134644 (March 1974). (N74-31024)**

The impact resistance of both room temperature and elevated temperature of Si_3N_4 and SiC ceramics was improved by the formation of energy absorbing surface layers. Low modulus layers were formed by using: (1) materials that microcrack as a result of thermal expansion anisotropy, (2) phases differing in thermal expansion, (3) materials that have phase transformations, and (4) vitreous coatings.

469. **Klein, M. J., and Metcalfe, A. G., "Ceramic Materials for Gas Turbine Environment", Solar Division of International Harvester Company, San Diego, California, Army Materials and Mechanics Research Center Contract Report No. AMMRC CTR 73-52 (December 1973). (AD 774 268)**

The effects of the additions of Al4.2 and 9.0 a/o in Si powders used to prepare reaction-sintered Si_3N_4 were investigated. The Al nitrided preferentially to form AlN. Bend strength and α-Si_3N_4 content were reduced by the additions.

470. **Land, P. L., Wimmer, J. M., Burns, R. W., Choudhury, N. S., "Compounds and Properties of the Si-Al-O-N System", Interim Report, 1 October 1973-1 October 1975, Technology, Inc., Dayton, Ohio, Air Force Materials Laboratory Contract Report No. AFML-TR-75-209 (April 1976). (AD-A026 520)**

Quasi-equilibrium diagram is presented for Si-Al-O-N compounds at 1800 C in 1 atm of N. X-ray diffraction spectra for several phases are given and the reaction and sintering processes are discussed. Theoretical densities are calculated from lattice parameter data on solid solutions.

471. **Lange, F. F., "Dense Si_3N_4 and SiC - Some Critical Properties for Gas Turbine Application" ASME Publication 72-GT-56 (1972).**

Presents current property data for both dense Si_3N_4 and SiC that are required to calculate thermal stresses: strength, modulus of elasticity, Poisson's ratio, thermal expansion, thermal conductivity, and specific heat.

472. **Lange, F. F., "Dense Si_3N_4: Interrelation Between Phase Equilibria, Microstructure and Mechanical Properties", Final Report, Westinghouse Research and Development Center, Pittsburgh, Pennsylvania, Office of Naval Research Contract Report (September 1976). (AD-A030 408)**

Mechanical properties of Si_3N_4 are reviewed from the standpoint of related fabrication parameters and compositional content. Microstructure of dense Si_3N_4 is governed by the phase relation of the constituents in the starting powder and these phase relations, in turn, govern the mechanical behavior.

473. **Lange, F. F., "Fabrication and Properties of Silicon Compounds, Task I. - Fabrication, Microstructure and Selected Properties of SiALON Compositions", Westinghouse Research Laboratories, Pittsburgh, Pennsylvania, Naval Air Systems Command Contract Report No. 74-9D4-SERAM-R1 (February 1974), pp 1-40. (AD 786 750)**

Si_3N_4-Al_2O_3 (<50 w/o) mixtures were hot pressed and sintered at temperatures up to 1650 C. Additions of MgO increased sintering kinetics. Thermal expansion, densification, and flexural strength were studied.

474. **Lange, F. F., "Fabrication of Silicon Compounds. Task III: Relative Resistance of Dense Silicon Nitride and Silicon Carbide to Surface Damage Introduced by Hertzian Contact Stresses", Westinghouse Research Laboratories, Pittsburgh, Pennsylvania, Naval Air Systems Command Contract Report No. 73-9D4-SERAM-R1 (April 1973). (AD 764 639)**

Surface damage was introduced into flexural-strength specimens of dense Si_3N_4 and SiC using spherical steel indenters and the specimens were then fractured in four-point loading. Si_3N_4 required $\sim$ four times the indenter load as SiC to introduce surface damage. After surface damage was introduced fracture due to subsequent external loading initiated from a portion of the sub-surface cone crack.

475. **Lange, F. F., "Phase Relations in the Si_3N_4-SiO_2-MgO System and Their Interrelations with Strength and Oxidation Resistance", Westinghouse Research and Development Center, Pittsburgh, Pennsylvania, Office of Naval Research Contract Report No. TR-9 (September 1976). (AD-A030 408)**

Phase equilibria studies at 1400-1750 C have established three important tie lines in the Si_3N_4-SiO_2-MgO system: (1) Si_3N_4-MgO, (2) Si_3N_4-Mg_2SiO_4, (3) Si_2N_2O-Mg_2SiO_4. Maximum strengths were obtained at 1400 C for MgO/SiO_2 molar ratios that approach zero and ifinity. Oxidation of these materials is discussed.

476. **Lange, F. F., "The Si_3N_4-SiC Composite System: Effect of Microstructure on Strength", Westinghouse Research Laboratories, Pittsburgh, Pennsylvania, Office of Naval Research Contract Report No. 72-9D4-KERAM-R1 (May 1972). (AD 743 510)**

Si_3N_4-SiC composite system was investigated to relate microstructure to strength-controlling factors: fracture energy, elastic modulus, and crack size. Composites formed by hot pressing included three different SiC dispersions (5 μm, 9 μm, and 32 μm) at several different volume fractions. Strength behavior of material containing two larger-size dispersions was controlled by crack size. Strength of 5 μm material was controlled by fracture energy and elastic modulus. Strength measurements at 1400 C and thermal conductivity measurements show that some composites are superior to hot-pressed Si_3N_4.

477. **Lange, F. F., "Strong, High-Temperature Ceramics", Westinghouse Research Laboratories, Pittsburgh, Pennsylvania, Office of Naval Research Contract Report No. 73-9D4-KERAM-P1 (February 1974). (AD 775 218)**

Hot-pressed Si_3N_4 and SiC are emphasized as strong, high-temperature ceramics that can withstand thermal cycling without failure and therefore be used in high-temperature structural applications. The relations between fabrication parameters, microstructure, and strength are presented for both materials and other structural considerations such as thermal shock, impact, and oxidation are reviewed. Current trends for obtaining improved and new materials are discussed.

478. **Lange, F. F., Singhal, S. C., and Kuznicki, R. C., "Phase Relations and Stability Studies in the Si_3N_4-SiO_2-Y_2O_3 Pseudo-Ternary System", Westinghouse Research and Development Center, Pittsburgh, Pennsylvania, Office of Naval Research Contract Report No. TR-6 (April 1976). (AD-A024 268)**

Composite powders were hot pressed to determine the phase relations within the Si_3N_4-SiO_2-Y_2O_3 pseudo-ternary system. Study of the four quarternary compounds identified showed they were unstable under oxidizing conditions. On the other hand, compositions within the Si_3N_4-Si_2N_2O-$Y_2Si_2O_7$ compatability triangle were extremely oxidation resistant.

479. **Lange, F. F., and Terwilliger, G. R., "Fabrication and Properties of Silicon Compounds", Westinghouse Research Laboratories, Pittsburgh, Pennsylvania, Naval Air Systems Command Contract Report No. 72-9D2-SERAM-R1 (January 1972). (AD 738 865)**

The strength of hot-pressed Si_3N_4 is dependent on the starting powder, the method used to prepare the powder for hot pressing, and the orientation of the crack plane relative to the hot-pressing direction. The material's elongated grain morphology is hypothesized to be responsible for its high fracture energy and directional properties. Study revealed that no single hot-pressing model adequately describes the hot-pressing behavior of Si_3N_4. The feasibility of hot pressing complex shapes using the powder vehicle technique was demonstrated. Dielectric properties were measured.

480. **Layden, G. K., "Process Development for Pressureless Sintering of SiAlON Ceramic Components", United Technologies Research Center, East Hartford, Connecticut, Naval Systems Command Contract Report No. UTRC/R75-912072 (January 1976). (AD-A022 696)**

Phase equilibria were studied in the system Si_3N_4-AlN-Al_2O_3-SiO_2. At temperatures above ~1750 C a broad two-phase field of liquids is in equilibrium with β'-SiAlON solid solutions. Studies were undertaken to exploit this two-phase field to effect a homogeneous transient liquid-phase sintering of β'-compositions.

481. **Leipold, M. H., Kapadia, C. M., and Kelkar, A. H., "Mechanical Behavior of Polycrystalline Ceramics: Brittle Fracture of SiC-Si_3N_4 Materials", Final Report, University of Kentucky, Lexington, National Aeronautics and Space Administration Contract Report No. NASA-CR-134732 (August 1974). (N75-10251)**

Final report of five-year contract with earlier annual reports listed in the Appendix. Slow crack growth does not occur in hot-pressed Si_3N_4 at room temperature, precluding use of proof testing to predict lifetime. Strain energy release rate remains constant with increase in loading rate. Also discussed is fracture toughness of various materials including Si_3N_4.

482. **Lenoe, E. M., and Neal, D. M., "Assessment of Strength - Probability - Time Relationships in Ceramics", Army Materials and Mechanics Research Center, Watertown, Massachusetts, Report No. AMMRC TR 75-13 (June 1975). (AD-A014 153)**

Compares various life computation procedures wherein realistic properties variability is treated. Predicted behavior of Si_3N_4 is studied and adequacy of estimating procedures is discussed.

483. **Lumby, R. J., Coe, R. F., and Lines, D. J., "The Development of Silicon Nitride to Achieve Higher Inlet Temperatures in Land-Based Gas Turbines", SAE Publication 720170 (January 1972).**

The introduction of the gas turbine engine into automotive transport will depend, in part, on the achievement of an efficient working cycle, that is, the operation of the turbine at inlet temperatures in excess of 1500 K. Of the candidate ceramic materials, Si_3N_4 is the most attractive because of its low expansion coefficient, good thermal shock resistance, and high strength at these temperatures. Fabrication and processing techniques for the production of Si_3N_4 are sufficiently advanced to enable material costs predictions to be made.

484. **Mary, J. P., Lotholary, P., Goursat, P., and Billy, M., "Process for the Manufacture of Parts With an Oxynitride Base", Kanner (Leo) Associated, Redwood City, California, National Aeronautics and Space Administration Contract Report No. NASA-TT-F-16440 (July 1975). Translation of French Patent Application No. 2,221,421 March 15, 1973. (N75-26030)**

Method of manufacturing refractory parts from a Si_2ON_2 base powder with a refractory metal oxide additive (~5% Al, Y, Mg, Be oxide).

485. **Masaki, Hideyuki, Nagoya, and Aichi, "Process for the Preparation of Sintered Ceramics on a Silicon Nitride Basis", Joint Publication Research Service, Arlington, Virginia, National Aeronautics and Space Administration Contract Report No. NASA-TT-F-16439 (July 1975). Translation of German Patent Application No. 2,353,093, October 23, 1973. (N75-29262)**

Method of manufacturing a heat-resistant, thermal-shock resistant, and high-strength Si_3N_4 material using various metal oxides, as MgO and Al_2O_3, and sintering at 1600-1800 C to form a spinel second phase.

486. **McLean, A. F., "The Application of Ceramics to the Small Gas Turbine", ASME Publication 70-GT-105 (May 1970).**

Ceramic materials are suggested as a means of achieving lower cost and higher inlet temperature in small gas turbine engines. Si_3N_4, SiC, and Li-Al-Si oxides are identified as promising materials for high-temperature turbine engine components.

487. **McLean, A. F., "The Ceramic Gas Turbine - A Candidate Powerplant for the Middle- and Long-Term Future", SAE Publication 760239 (February 1976).**

Review of Ford's ceramic gas turbine program. (See entry nos. 489-498)

488. **McLean, A. F., "Development Progress on Ceramic Turbine Stators and Rotors", ASME Publication 75-GT-11 (1975).**

Review of design, fabrication, and thermal testing of Si_3N_4 components. Also includes results on high-temperature testing of stators and reviews spin-testing techniques.

489. **McLean, A. F., Fisher, E. A., and Harrison, D. E., "Brittle Materials Design, High Temperature Gas Turbine", Interim Report, 1 July 1971-31 December 1971, Ford Motor Company, Dearborn, Michigan, Army Materials and Mechanics Research Center Contract Report No. AMMRC CTR 72-3 (March 1972). (AD 894 052L)**

In the vehicular gas turbine project, ceramic turbine components of improvised design were fabricated and engine testing was started. During the first contract reporting period, Si_3N_4 turbine stators of the new design have shown considerably improved durability in testing to date. New design Si_3N_4 nose cones were fabricated by injection molding. Design studies on ceramic turbine rotors have shown that computed operating stresses can be withstood by dense SiC and dense Si_3N_4. Development programs were started to fabricate rotors in these materials.

Work on the stationary turbine project has concentrated on materials evaluation and initial design of ceramic stator vanes. Maximum calculated vane stresses were reduced 40% by decreasing the stator vane chord. The strength of hot-pressed Si_3N_4, one of the candidate materials, has been significantly improved. A variety of microstructural details of this material have been identified. Physical property data were obtained on hot-pressed Si_3N_4.

490. **McLean, A. F., Fisher, E. A., and Bratton, R. J., "Brittle Materials Design, High Temperature Gas Turbine", Interim Report, 1 January 1972-30 June 1972, Ford Motor Company, Dearborn, Michigan, Army Materials and Mechanics Research Center Contract Report No. AMMRC CTR 72-19 (September 1972). (AD 905 043L)**

In the vehicular turbine project, the improved second generation (Design B) stationary ceramic components made of reaction-bonded Si_3N_4 have undergone initial engine tests successfully. A computer program has been developed to determine heat transfer in the rotor, attachment, and shaft assembly. A design study was completed for the attachment of the rotor to the shaft. A complete integral rotor has been fabricated by CVD of SiC, although material quality needs improvement. An etching technique has been developed permitting microstructure study of any form of Si_3N_4, and significant determinations were made of ceramic material properties.

In the stationary turbine project, a first generation 3-piece vane assembly was designed and analyzed. A complete set of Si_3N_4 airfoil vanes was fabricated. Engineering properties of Si_3N_4 and SiC have been characterized. A better understanding of the effects of microstructure on properties of hot-pressed Si_3N_4 was obtained. Data was obtained on static oxidation kinetics and corrosion-erosion behavior.

491. **McLean, A. F., Fisher, E. A., and Bratton, R. J., "Brittle Materials Design, High Temperature Gas Turbine", Interim Report, 1 July 1972-31 December 1972, Ford Motor Company, Dearborn, Michigan, Army Materials and Mechanics Research Center Contract Report No. AMMRC CTR 73-9 (March 1973). (AD 910 446L)**

In the vehicular turbine project, steady state and transient stresses were determined for a monolithic turbine rotor of hot-pressed Si_3N_4. A new rotor concept, using both hot-pressed and reaction-sintered Si_3N_4, has been analyzed for steady-state stresses; work on bonding the two materials appears promising. Improvements in CVD SiC rotors include the forming of hoops of sufficient thickness and the production of material of considerably improved purity. Blade cracking of the first stage ceramic stator was duplicated on a thermal test rig, leading to improved durability through a change in the blade design. Some fabrication variables of reaction-sintered Si_3N_4 were studied, which indicate methods for material improvement.

In the stationary turbine project, a model of the 3-piece stator vane assembly demonstrated that design integrity was maintained when differential motion exceeded design limits fivefold. The 3-dimensional finite element stress and heat transfer analytical program has been applied to rotor blades, and preliminary results are presented. Statistical data treatment has been applied to hot-pressed Si_3N_4 and additional property data plus corrosion testing results are presented for hot-pressed SiC. It was found necessary to design and construct a new static rig, delaying testing under turbine conditions until August.

492. **McLean, A. F., Fisher, E. A., and Bratton, R. J., "Brittle Materials Design, High Temperature Gas Turbine", Interim Report, 1 January 1973-30 June 1973, Ford Motor Company, Dearborn, Michigan, Army Materials and Mechanics Research Center Contract Report No. AMMRC CTR 73-32 (September 1973). (AD-914 451L)**

In the vehicular turbine project, a more refined heat transfer and stress analysis was performed for the monolithic hot-pressed Si_3N_4 rotor. Methods of fabricating duo-density Si_3N_4 rotors were evaluated, with several rotors being made; the best of these failed at 50,500 rpm during spin testing. Revised design stators demonstrated improved durability, although cracking has not been completely eliminated. Creep resistance of reaction-sintered Si_3N_4 has been considerably improved by decreasing Ca-containing impurities. The strength of reaction-sintered Si_3N_4 has been increased by the use of small amounts of H added to the N atmosphere.

In the stationary turbine project, stress and heat transfer analyses were completed for the stator vane assembly system. The 3-dimensional stress analysis program has been expanded to include steady state and transient heat transfer capability. Installation of the static test rig for evaluating stator vanes under turbine conditions has been completed. Additional information about the properties of hot-pressed Si_3N_4 and SiC has been determined, and the microstructure of hot-pressed SiC was studied in detail.

493. **McLean, A. F., Fisher, E. A., and Bratton, R. J., "Brittle Materials Design, High Temperature Gas Turbine", Interim Report No. 5, 1 July 1973-31 December 1973, Ford Motor Company, Dearborn, Michigan, Army Materials and Mechanics Research Center Contract Report No. AMMRC CTR 74-26 (April 1974). (AD 920 691L)**

In the vehicular turbine project, Weibull theory was utilized to predict failure probabilities of monolithic hot-pressed Si_3N_4 turbine rotors, including the effects of varying disk contours. Good agreement with theory resulted from strength testing of Si_3N_4 bars and disks. Processing parameters were established for the fabrication of multi-density rotors, and a number of prototype rotors were spin tested. Thermal response of stator vanes during engine operation was determined directly using a quartz window in a stator test rig. Improvements in properties were made for both injection molded and slip cast reaction-sintered Si_3N_4.

In the stationary turbine project, a major objective was achieved when the first static rig test of hot-pressed Si_3N_4 stator vanes was completed at temperatures up to 2200 F. Although some vanes failed due to out-of-tolerance final machining of critical interfaces, it was encouraging that two vanes which were subjected to the highest temperatures and most severe transient effects were not damaged. Additional information was also generated on the properties and corrosion resistance of hot-pressed Si_3N_4.

494. **McLean, A., F., Fisher, E. A., and Bratton, R. J., "Brittle Materials Design, High Temperature Gas Turbine", Interim Report No. 6, 1 January 1974-30 June 1974, Ford Motor Company, Dearborn, Michigan, Army Materials and Mechanics Research Center Contract Report No. AMMRC CTR 74-59 (September 1974). (AD-B000 384L)**

In the vehicular turbine project, 3-dimensional stress analysis programs are being developed and applied to turbine rotors and stators. Improvements have been made in the fabrication of duo-density Si_3N_4 rotors. A major objective was reached with the completion of a 50-hour cyclic engine test of ceramic hot-flow path components. A SiC combustor tube was tested in a combustor rig for 50 hours, including 6 hours at an outlet temperature of 2500 F. Non-destructive evaluation techniques have been applied to the fabrication of ceramic components resulting in the elimination of defective parts at an early stage in processing.

In the stationary turbine project, considerable design effort was expended on the modification of the rotating test turbine for the high-temperature testing to meet program objectives. The static test rig was rebuilt for 2500 F peak temperature operation, and 5 cycles were run to 2300 F to establish control parameters. Damage to the new ceramic duct section and to the mixer caused testing to be stopped. The Si_3N_4 and SiC stator vane assemblies being tested were apparently undamaged. A rotor blade configuration was analyzed by the 3-dimensional stress analysis program and the results are presented.

495. **McLean, A. F., Fisher, E. A., Bratton, R. J., and Miller, D.G., "Brittle Materials Design, High Temperature Gas Turbines", Interim Report No. 7, 1 July 1974-31 December 1974, Ford Motor Company, Dearborn, Michigan, Army Materials and Mechanics Research Center Contract Report No. AMMRC CTR 75-8 (April 1975). (AD-B004 531L)**

In the vehicular turbine project, a major program milestone, comprising a 100-hour durability test of the stationary ceramic hot flow path components in an engine was completed. In the fabrication of ceramic turbine rotors, significant improvement in bonding the components of the silicon nitride duo-density rotor resulted when hot pressing of the shaped hub was combined with press bonding to the blade ring. Spin testing of seven hot-pressed silicon nitride rotor hubs, with burst speeds ranging from 102,000 to 120,000 rpm, confirmed that this material was adequate for rotor requirements. A silicon carbide combustor tube has been successfully tested in a combustor rig for a total of 171 hours, including 20 hours at an outlet temperature of 2500 F. A redesigned ceramic flow path, Design D, was conceived using common one-piece stators and common rotors in both first and second stage locations. Through variations in particle size distribution, it was found that injection molded reaction-sintered silicon nitride of 2.7 g/cm^3 density (84.5% of T.D.) could be made. The effect of oxidation on lower density forms of reaction-sintered silicon nitride was evaluated.

In the stationary turbine project, static rig testing of hot-pressed Si_3N_4 and SiC stator vanes up to 2500 F was initiated. Cracks were observed visually on two of the four SiC vanes during the third cycle, but the vanes remained functional. During the fifth cycle, the metal combustor basket imploded, throwing metal debris into the vanes, followed by a temperature excursion to 3000 F and a rapid quench to 600 F under choked flow conditions. Following this accident, it was found that all four SiC vanes had been shattered. One of the four Si_3N_4 vanes was cracked, while the remaining three vanes were still intact, an encouraging example of ceramic material survival under unexpected catastrophic conditions. The static test rig is being modified and rebuilt for the continuation of 2500 F testing. Additional tensile strength and creep tests were performed on hot-pressed Si_3N_4.

496. **McLean, A. F., Fisher, E. A., Bratton, R. J., and Miller, D. G., "Brittle Materials Design, High Temperature Gas Turbine", Interim Report No. 8, 1 January 1975-30 June 1975, Ford Motor Company, Dearborn, Michigan, Army Materials and Mechanics Research Center Contract Report No. AMMRC CTR 75-28 (October 1975). (AD-B010 248L)**

In the vehicular turbine project, design work was completed and tooling ordered for a revised Design D Si_3N_4 duo-density turbine rotor using radially stacked airfoil sections which reduced blade stresses by 16%. Press bonding of duo-density rotors continues to show excellent bonding between the hot-pressed hub and the reaction-sintered blade ring when hub-forming and bonding are accomplished in the same operation. Two hot-pressed Si_3N_4 hubs were successfully tested through ten cycles to 1950 F and 35,000 rpm in the turbine rotor test rig with no observable deterioration in the curvic coupling rotor-to-shaft attachment. Stators of 2.55 g/cm^3 density Si_3N_4 were injection molded which were free from flaws as determined visually and by X-ray radiography. Further development of 2.7 g/cm^3 density (84.5% T.D.) injection molded silicon nitride resulted in improved moldability; test samples nitrided in an atmosphere of 4% H_2/96% N_2 had an average modulus of rupture of 43.2 ksi. This material will be used for molding of engine components.

In the stationary turbine project, a decision was made to de-emphasize the 30 Mw size turbine demonstration of ceramic stator vanes and to focus available efforts on static rig testing. The static rig was rebuilt following catastrophic failure, and incorporates a new metal combustor with additional air cooling as well as other improvements. Tensile testing of Si_3N_4 continues, with the development of a method of powder support for the specimens which considerably improved alignment. Long-term static oxidation testing of hot-pressed Si_3N_4 resulted in strength degradation, due to the formation of $MgSiO_3$ which chemically attacks the Si_3N_4. Hot-pressed Si_3N_4 made with yttria additives was found to have poor oxidation resistance at 1800 F, although oxidation resistance was good when measured at higher temperatures.

497. **McLean, A. F., Baker, R. R., Bratton, R. J., and Miller, D. G., "Brittle Materials Design, High Temperature Gas Turbine", Interim Report No. 9, 1 July 1975-31 December 1975, Ford Motor Company, Dearborn, Michigan, Army Materials and Mechanics Research Center Contract Report No. AMMRC CTR 76-12 (April 1976). (AD-B012 108L)**

The demonstration of uncooled brittle materials in structural applications at 2500 F is the objective of this program. Ford Motor Company, the contractor, will utilize a small vehicular gas turbine while Westinghouse, the subcontractor, will use a large stationary gas turbine. Both companies had in-house research programs in this area prior to this contract.

A significant achievement in the vehicular turbine project was the successful engine test, 175 hours at 1930 F, of a Si_3N_4 stator. Two stator vanes survived 1000 cycles to 2500-2600 F plus 3720 cycles to 2900 F in the thermal shock rig. A poor quality partially bladed duo-density Si_3N_4 turbine rotor was tested for two hours with excursions to 1920 F and 33,600 rpm before failure. Two ceramic rotors with short blades were successfully proof spun to 64,000 rpm, cold, as part of a program to test ceramic rotors with phased increases in blade height. One of seven hot-pressed rotor hubs, spun to determine material strength, achieved 111,800 rpm before failure.

Reduction of the MgO content increased the hot strength of the hot-pressed Si_3N_4 rotor hub material. Improvements in the nitriding cycle and injection molding process produced 2.7 g/cm^3 test bars with a characteristic four-point bend strength of 44.3 ksi with a Weibull slope of 6.8. A stress rupture test on 2.7 g/cm^3 injection molded material was suspended without failure after 1159 hours at 2300-2400 F and stresses in four-point bending of up to 35 ksi.

The goal of the stationary turbine project is to demonstrate ceramic stator vanes operating at a maximum temperature of 2500 F for 100 cycles simulating peaking service conditions. The original goal to accomplish this in an advanced gas turbine engine was revised to complete the demonstration in a static test rig. Sixty cycles have been completed in the static test rig with the total time at temperature (2500 F) approaching three hours and three of the original eight vanes remain crack free.

498. **McLean, A. F., and Baker, R. R., "Brittle Materials Design, High Temperature Gas Turbine", Interim Report No. 10, 1 January 1976-30 June 1976, Ford motor Company, Dearborn, Michigan, Army Materials and Mechanics Research Center Contract Report No. AMMRC CTR 76-31 (October 1976).**

In the stationary gas turbine project at Westinghouse, the test of ceramic stator vanes in a static rig for 100 cycles up to temperatures of 2500 F has been completed.

A significant achievement, in the vehicular turbine project at Ford, was the test of a partially bladed duo-density silicon nitride turbine rotor in an experimental high temperature gas turbine engine up to a speed of 52,800 rpm and turbine inlet temperature of 2650 F before failure on a subsequent run. Two rotors, with blades of 10% length, were successfully tested for 45 minutes at 32,000 rpm and 2000 F turbine inlet temperature. Cold spin test results of nine hot-pressed Si_3N_4 rotor hubs correlated well with analytical predictions based on Weibull MOR data from 140 test bars cut from five additional hubs. Testing of the stationary components continued with a "Refel" SiC combustor tube successfully accumulating over 200 hours in the steady-state test rig, equivalent to the prescribed 200-hour engine duty cycle goal. Twenty-six hours and 40 minutes of this testing was at a turbine inlet temperature of 2500 F. A reaction-bonded SiC stator accumulated 147 hours of operation at 1930 F and remains crack free. Testing of stationary components at turbine inlet temperatures up to 2500 F continued with over nine hours of test time accumulated without failures.

An important fabrication development to make duo-density turbine rotors in three pieces was conceived and demonstrated a significant reduction of applied loads during hot-press bonding generally eliminating blade and rim cracking.

Modulus of Rupture tests were conducted on hot-pressed Si_3N_4 to investigate the effects of surface finish, post machining heat treatments and process variations. Bending stress rupture tests on 15 specimens resulted in no time dependent failures for this material up to 2200 F. Twelve of the tests were suspended, without failure, after 200 plus hours at stresses of 20-30 ksi and temperatures of 1900-2200 F. The key to uniform microstructure, fine porosity, and associated high strengths is the control of localized nitriding exotherms so that no silicon melt out occurs.

499. **Mead, A. P., "The Determination of Oxygen and Nitrogen in Some Nitrides and Carbides by Inert Gas Fusion Using an Impulse Heating Furnace", Atomic Energy Research Establishment, Harwell, England, Research Report No. AERE-R-6537 (November 1970).**

An inert gas fusion technique using an impulse heating furnace at 2600-2700 C and a gas-solid chromatographic method of gas measurement is described for the simultaneous determination of O and N in nitrides of Si, Ti, Zr, and the carbides of Ti and W. A single determination of O and N requires $\sim$10 minutes.

500. **Messier, D. R., and Wong, P., "Duplex Ceramic Structures: Interim Report No. 1, Kinetics of Fabrication of Silicon Nitride by Reaction Sintering", Army Materials and Mechanics Research Center, Watertown, Massachusetts, Research Report No. AMMRC TR 72-10 (March 1972). (AD 742 669)**

The reaction-sintering process for the fabrication of Si_3N_4 was investigated over the temperature range from 1150-1450 C. The effects of Fe and O impurities and of particle size were determined. The kinetics of the reaction between pure (99.99%) Si powder compacts and N were parabolic.

501. **Messier, D. R., and Wong, P., "Effect of Processing Conditions on Microwave Dielectric Properties of Reaction-Sintered Silicon Nitride", Army Materials and Mechanics Research Center, Watertown, Massachusetts, Report No. AMMRC TR 76-3 (February 1976). (AD-A021 539)**

Unreacted Si at levels >0.5-0.6 w/o seriously degrade the dielectric properties of reaction-sintered Si_3N_4. The use of fine particle size Si and various oxide additives were both effective in reducing unreacted Si. Two independent measurements of dielectric properties were in good agreement. The properties appear adequate for radome applications up to 1000 C.

502. **Messier, D. R., and Wong, P., "Silicon Nitride: A Promising Material for Radome Applications", Army Materials and Mechanics Research Center, Watertown, Massachusetts, Research Report No. AMMRC TR 74-21 (September 1974). (AD 787 255)**

Dielectric properties of various reaction-sintered and hot-pressed Si_3N_4 specimens were measured at 10 GHz at room temperature, 1000 F, and 2000 F. Dielectric constant values ranged from 5.5 to 9.3, and tangent loss values from 0.001 to 0.16. The major detrimental impurity was identified as residual unreacted Si.

503. **Moran, H. D., and Hanby, K. R., "Silicon Nitride for Gas Turbine Applications. A Comparison of Selected Strategic Materials Technologies in U.S.A. and U.S.S.R.", Battelle's Columbus Laboratories, Columbus, Ohio, Advanced Research Projects Agency Order-2371 (April 1973). (AD 760 329)**

Results of a survey to determine what, if any, ceramic engine development using Si_3N_4 was being pursued in the Soviet Union. There is evidence of a strong capability for basic research, but no evidence of a program to evaluate Si_3N_4 in gas turbine engines or ceramic components of any kind.

504. **Morgan, P.E.D., "Production and Formation of Si_3N_4 from Precursor Materials", Final Annual Report, March 1973-December 1973. The Franklin Institute Research Laboratories, Philadelphia, Pennsylvania, Office of Naval Research Contract Report No. FIRL-A-C3316 (March 1974). (AD 778 373)**

A region of rapid densification, coincident with the transformation of amorphous to α-Si_3N_4 during hot pressing at 1490 C, has been seen in highly pure material made from $Si(NH)_2$ by the liquid NH_3 route. A tentative explanation of the phase relationships of α- and β-Si_3N_4 is presented based on conflicting σ and π orbital overlap requirements in multiply bonded Si and N.

505. **Morgan, P.E.D., "Research on Densification, Character and Properties of Dense Silicon Nitride", Franklin Institute Research Laboratories, Philadelphia, Pennsylvania, Office of Naval Research Contract Report No. FIRL-A-C3316 (March 1973). (AD 757 748)**

Reactive hot pressing of $Si(NH)_2$ produced Si_3N_4 of up to 85% theoretical density. The presence of β-Si_3N_4 in the product indicated low O activity during the process.

506. **Morgan, P.E.D., "Study of Pi-Bonding in Silicon Nitride and Related Compounds", Franklin Institute Research Laboratories, Philadelphia, Pennsylvania, Office of Naval Research Contract Report No. FIRL-F-C2429 (August 1974). (AD 784 997)**

The degree and nature of (p-d) pi-bonding in various Si_3N_4 compounds was studied. On the basis of relative bond lengths and angular relationships and assuming that both α- and β-Si_3N_4 compounds are pure, it is predicted that the β-form is more stable, only by a very small amount.' Some implications of Si-Al-O-N bonding are reviewed.

507. **Nessler, C. G., "Gas Turbine Ceramic Vane Testing", SAE Publication 740235 (February 1974).**

Relevant material properties of prototype hot-pressed Si_3N_4 and SiC vanes were determined. Primary limitations revealed were a propensity for sudden thermal fatigue crack propagation and low impact damage resistance.

508. **Nomata, Y., and Inoue, Z., "Decomposition Temperature of Silicon Nitride in the System Si_3N_4-C-N_2 (1 atm)", Scientific Translation Service, Santa Barbara, California, National Aeronautics and Space Administration Contract Report No. NASA-TT-F-16450 (July 1975). Translation of Yogyo Kyokai Shi, 81 (1973), pp 441-444. (N75-28227)**

Direct measurements of decomposition temperature of Si_3N_4 were performed in the highly pure Si_3N_4-C-N_2 system at 1 atm. The decomposition temperature obtained, 1839 C ± 14 C, is the lowest yet reported. Briefly describes β-Si_3N_4 single crystals that were obtained.

509. **Oyama, Y., and Kamigaito, O., "Sintered Bodies of Silicon Nitride - Alumina System", Army Foreign Science and Technology Center, Charlottesville, Virginia, Report No. FSTC-HT-23-1407-73 (June 1973). Translation of Yogyo Kyokai Shi, 80 (1972), pp 29-38, 327-336. (AD-B000 153L)**

Characteristics of the Si_3N_4-Al_2O_3 system sintered materials are discussed. Oxidation resistance of the Al_2O_3 additive in the sintered Si_3N_4 was analyzed. Chemical reactions and processes used to produce the sintered material are described. Tables of the physical and mechanical properties are presented.

510. **Paluszny, A., "Designing with High Temperature Ceramics", ASME Publication 75-DE-28 (1975).**

Various aspects of the design technology being developed for ceramic materials within the framework of the Ford/ARPA contract are outlined. (See entry nos. 489-498). Analytical and statistical design tools and design methodology are discussed in detail. Correlation of analytical strength predictions with controlled tests of simplified structures is presented in support of statistical theories, and use of statistical analysis in rotor design is discussed.

511. **Parker, R. J., and Zaretsky, E. V., "Fatigue Life of High-Speed Ball Bearings with Silicon Nitride Balls", National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio, Technical Memorandum No. NASA-TM-X-71576 (1974). (N74-28958)**

Hot-pressed Si_3N_4 was evaluated as a rolling element bearing material at 55 C using the five-ball fatigue tester. Fatigue life was equal to typical bearing steels and much greater than that of other ceramics and cermets.

512. **Parker, R. J., and Zaretsky, E. V., "Rolling-Element Fatigue Life of Silicon-Nitride Balls", National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio, Technical Note No. NASA-TN-D-7794 (October 1974). (N74-34889)**

Hot-pressed Si_3N_4 balls were tested under rolling contact conditions in the five-ball fatigue tester and fatigue lives compared with those for typical bearing steels, AISI 52100 and AISI M-50. Extrapolation of experimental results indicated that the Si_3N_4 fatigue life was comparable to or exceeded that of the steels and was considerably greater than the other ceramics or cermets tested.

513. **Parker, R. J., and Zaretsky, E. V., "Rolling-Element Fatigue Life of Silicon Nitride Balls - Preliminary Test Results", National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio, Technical Memorandum No. NASA-TM-X-68174 (November 1972). (N73-15922)**

Hot-pressed Si_3N_4 was evaluated as a rolling-element bearing material in a five-ball fatigue tester at 800,000 psi and a race temperature of 55 C. Fatigue spalls in Si_3N_4 resembled those in typical bearing steels. The 10% fatigue life of Si_3N_4 was ∿1/8 to 1/5 that of typical bearing steels (52100 and M-50) and the load capacity was ∿1/3 but considerably higher than previously tested ceramic materials.

514. **Parker, R. J., and Zaretsky, E. V., "Silicon Nitride Used as a Rolling-Element Bearing Material", National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio, NASA Technical Brief B-75-10134 (July 1975).**

Fatigue life of hot-pressed Si_3N_4 approaches that of AISI 52100 steel. The usefulness of Si_3N_4 balls in contact with steel races is limited. There has been some success in using Si_3N_4 for both balls and races.

515. **Platts, D. R., Kirchner, H. P., and Gruver, R. M., "Strengthening of Oxidation Resistant Materials for Gas Turbine Applications", Ceramic Finishing Company, State College, Pennsylvania, National Aeronautics and Space Administration Contract Report No. NASA CR-121002 (September 1972). (N73-11796)**

Compressive surface layers were formed on hot-pressed SiC by quenching and on hot-pressed Si_3N_4 by carburizing treatments. Impact resistance of SiC at 2400 F was improved and some improvement of Si_3N_4 was noted under the same conditions.

516. **Potter, N. D., and Piper, G., "Thermodynamic Properties of High Temperature Materials", Philco-Ford Corporation, Newport Beach, California, Air Force Office of Scientific Research Contract Report No. AFOSR-74-0799TR (March 1974). (AD 780 111)**

Mass spectrometric study of the Si-N vapor system showed the presence of the binary species Si_2N, having a heat of formation of 83 ± 4 kcal/mol. No ternary Si-N-O or Si-C-N species were found. The vaporization behavior of Si_3N_4 was found to be quite complex.

517. **Reddecliff, J. M., "Silicon Nitride Ball Bearing Demonstration Test", Pratt and Whitney Aircraft, West Palm Beach, Florida, Office of Naval Research Contract Report No. PWA-FR-6995 (May 1975). (AD-A012 526)**

A 35 mm bore angular contact ball bearing having M50 tool steel races and hot-pressed Si_3N_4 balls was tested at speeds to 75,500 rpm. The bearing ran smoothly throughout 32 hours of accumulated time. Heat generation was 10-20% less than that of a comparable bearing with steel balls and the Si_3N_4 bearing required 30% less axial load at the inception of ball skid.

518. **Rhodes, W. H., Berneburg, P. L., Cannon, R. M., Jr., and Steele, W. C., "Microstructure Studies of Polycrystalline Refractory Oxides", Summary Report March 1972-April 1973, Avco Corporation, Systems Division, Lowell, Massachusetts, Naval Air Systems Command Contract Report (April 1973). (AD 760 353)**

Initial experiments on press forging Si_3N_4 are reported.

519. **Rhodes, W. H., and Cannon, R. M., Jr., "High Temperature Compounds for Turbine Vanes", Avco Corporation, Systems Division, Lowell, Massachusetts, National Aeronautics and Space Administration Contract Report No. NASA CR-120966 (September 1972). (N72-31780)**

Fabrication and microstructure control studies were conducted on SiC, Si_3N_4, and composites based on the compounds. Charpy impact tests to 2400 F showed coated Si_3N_4 and Si_3N_4 derived from α-Si_3N_4 powder, and other materials had promising strengths. Improved 2000 F–100 hours strengths were obtained by increasing the grain size (to at least 5 μm), the density, and possibly the phase purity of Si_3N_4. At 2400 F where a grain-boundary phase controls strength these parameters became less important.

520. **Rhodes, W. H., and Cannon, R. M., Jr., "Microstructure Studies of Polycrystalline Refractory Compounds", Summary Report May 1973-April 1974, Avco Corporation, Systems Division, Lowell, Massachusetts, Naval Air systems Command Contract Report (June 1974). (AD 782 647)**

Emphasizes work on Al_2O_3 but reports on forging of Si_3N_4. Densities were >98% with strengths near those for hot-pressed material.

521. **Richman, M. H., "An Investigation of the Effect of Processing Parameters on the Reaction Sintering of Silicon Nitride", Brown University, Providence, Rhode Island, Army Research Office Contract Report No. ARO-10618.1-MC (1975). (AD-A012 954)**

A detailed and systematic study of the processing parameters on microstructure and the effect of well characterized microstructural morphology on the bulk properties of reaction-bonded Si_3N_4 is presented. Desirable and undesirable microconstituents were investigated.

522. **Rockett, T. J., Gielisse, P. J., Damani, O. B., Kulkarni, K., and Smith, P. W., "Performance Evaluation of Ceramic Materials and Aspects of Surface Preparation for Gas Bearings", Rhode Island University, Kingston, Office of Naval Research Contract Report No. 98-04-4046C (December 1975). (AD-A027 700)**

Evaluation of friction and wear properties showed that Si_3N_4 yielded more wear debris than B_4C. Surface preparation for gas bearings was studied in depth.

523. **Sanders, W. A., and Probst, H. B., "Evaluation of Oxidation Resistant Nonmetallic Materials at 1204 C (2200 F) in a Mach 1 Burner", National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio, Technical Note No. NASA-TN-D-6890 (August 1972). (N72-29565)**

Specimens of 23 oxidation resistant, nonmetallic materials, including Si_3N_4 (two very high density and one 20% porous) were systematically exposed in a high gas velocity burner in a gas turbine engine. Exposure to Mach 1 and Mach 0.5 hot gas streams resulted in specimen temperatures of 1204 C (2200 F). Si_3N_4 and SiC exhibited the most promising behavior surviving all exposures including Mach 1 for 120 cycles (10 hours).

524. **Sanders, W. A., and Probst, H. B., "Behavior of Ceramics at 1200 C in a Simulated Gas Turbine Environment", SAE Publication 740240 (March 1974).**

Summarizes testing programs at NASA Lewis Research Center on 23 ceramics. SiC and Si_3N_4 were identified as outstanding in resistance to oxidation and thermal stress and were chosen for further testing in simulated vane shape geometry. Certain SiC and Si_3N_4 materials were superior to others based on several criteria including weight and dimensional changes, metallography, fluorescent penetration analysis, X-ray diffraction analysis, and failure mode.

525. **Schlike, P. W., "Advanced Ceramic Seal Program (Phase I)", Final Report, 15 August 1972-30 September 1973, Pratt and Whitney Aircraft, East Hartford, Connecticut, Naval Air Propulsion Test Center Contract Report No. PWA-6635 (October 1973). (AD 781 004)**

Considers ceramic materials including reaction-sintered and hot-pressed Si_3N_4 for seal materials. Suggests stabilized ZrO_2 and hot-pressed SiC are the best candidates.

526. **Sedlacek, R., and Jones, R. L., "A Study of Properties and Behavior of High Temperature Gas Turbine Materials", Stanford Research Institute, Melo Park, California, Army Materials and Mechanics Research Center Contract Report No. AMMRC CTR 74-19 (March 1974). (AD 919 326L)**

Expanded ring tests were performed on specimens machined from hot-pressed Si_3N_4 in 30% RH air at 70 F ± 2 F. Results indicated there was no significant variation of mean fracture strength for specimens tested at stress rates between 1.5×10^2 psi/sec and 5×10^5 psi/sec.

527. **Sharp, J. V., Evans, A. G., and Hudson, B., "Electron Diffraction Data for Silicon Nitride", Atomic Energy Research Establishment, Harwell, England, Report No. AERE-R-7319 (December 1972).**

Electron diffraction data are presented for both α- and β- phases of Si_3N_4. Interplanar spacings and angles, relative spot intensities, and two beam extinction distances were computed and a range of typical diffraction patterns were prepared for both phases. Unambiguous identification of the structures by this method is possible only under certain conditions.

528. **"Silicon Nitride as a Bearing Material", Proceedings of Program Review on Silicon Nitride as a Bearing Material, held at King of Prussia, Pennsylvania, 9-10 July 1974, Naval Air systems Command, Washington, D. C. (July 1974). (AD-B002 315L)**

529. **Simonen, F. A., and Duckworth, W. H., "Analysis of Ceramic Materials for Impact Members in Isotropic Heat Sources", Battelle's Columbus Laboratories, Columbus, Ohio, U. S. Energy Research and Development Administration Contract Report No. BMI-X-670 (May 1976).**

Assesses materials including hot-pressed Si_3N_4 as encapsulants for PuO_2 ceramic fuel. Materials limitations include impact resistance, weight, and difficulties in fabrication.

530. **Singhal, S. C., "Corrosion Behavior of Silicon Nitride and Silicon Carbide in Turbine Atmospheres", Proceedings of the 1972 Tri-Service Conference on Corrosion, Houston, Texas, 5-7 December 1972, Metals and Ceramics Information Center, Columbus, Ohio, Report No. MCIC 73-19 (1973), pp 245-247. (AD 771 345)**

Corrosion behavior of hot-pressed Si_3N_4 and SiC in the temperature range 1800-2500 F is discussed. Static oxidation and dynamic corrosion tests were performed. The oxidation of both Si_3N_4 and SiC followed parabolic rate laws during initial stages of oxidation with the formation of stable SiO_2 layers on their surfaces.

531. **Singhal, S. C., "Corrosion-Resistant Structural Ceramic Materials for Gas Turbines", Proceedings of 1974 Gas Turbine Materials in the Marine Environment Conference, edited by J. W. Fairbanks and I. Machlin, Metals and Ceramics Information Center, Columbus, Ohio, Report No. MCIC 75-27 (June 1975), pp 311-321. (AD-A013 436)**

Oxidation and corrosion-erosion behavior of high-strength hot-pressed Si_3N_4 and SiC in gas turbine environments up to 1370 C is reviewed and discussed. The oxidation behavior is governed by the impurities and various additives present. Both materials resist deterioration by high concentrations of Na, V, and S. The excellent corrosion resistance is due to the formation of protective surface layers of silica and/or silicates.

532. **"Structural Ceramics", National Materials Advisory Board, Washington, D. C., Report No. NMAB-320 (1975). (AD-A015 879)**

The objectives of this study were to evaluate the advances in the uses of ceramics, including Si_3N_4, as engineering load carrying structural materials and to make recommendations for support of future developments, particularly for the U. S. Department of Defense and the National Aeronautics and Space Administration, and generally for the nation as a whole.

533. **Sundberg, D. V., "Ceramic Roller Bearings for High-Speed and High-Temperature Applications", SAE Publication 740241 (1974).**

Rolling contact fatigue machines were used to test elemental fatigue of bearings made with Si_3N_4 rolling elements and M50 CVM steel or Si_3N_4 races. The bearings were tested at speeds $\leqslant$500,000 DN (bore diam times rpm) under heavy loads to give accelerated test conditions and showed promise.

534. **Terwilliger, G. R., and Lange, F. F., "Fabrication and Properties of Silicon Compounds, Task II: Pressureless Sintering of Si_3N_4", Westinghouse Research Laboratories, Pittsburgh, Pennsylvania, Naval Air Systems Command Contract Report No. 73-9D4-SERAM-R1 (April 1973). (AD 764 639)**

Si_3N_4 containing 5 w/o MgO can be densified to 90% of theoretical without application of pressure if the proper time/temperature schedule is followed. Shrinkage is consistant with liquid-phase sintering. Above 1650 C decomposition reduces densification.

535. **Tomas, J., "Optimum Design of a Ceramic Turbine Wheel", SAE Publication 760241 (February 1976).**

Optimum turbine wheel geometry was calculated for two materials—hot-pressed Si_3N_4 and densified SiC. Minimum failure probability was determined by coupling the mathematical program technique with finite element and finite differences methods. Results indicate an improvement in material quality is necessary.

536. **Torti, M. L., Weaver, G. Q., and Richerson, D. W., "Hot Pressed Silicon Nitride for Gas Turbine Applications", ASME Publication 72-GT-19 (January 1972).**

High strength combined with good oxidation and thermal shock resistance make hot-pressed Si_3N_4 a most promising candidate for advanced gas turbine hot components. This form of Si_3N_4 has flexural strengths of 110,000 psi at room temperature and 60,000 psi at 1200 C. A recent experimental version of the system exhibited strengths as high as 145,000 psi at room temperature and 100,000 psi at 1200 C.

537. **Tripp, W. C., Hinze, J. W., Mendiratta, M. G., Duff, R. H., and Hampton, A. F., "Internal Structure and Physical Properties of Ceramics at High Temperatures", Systems Research Laboratories, Inc., Dayton, Ohio, Aeronautical Research Laboratory Contract Report No. ARL-75-0130 (June 1975). (AD-A013 167)**

Included are results on the oxidation behavior or SiC, Si_3N_4, and Si at high temperatures. Oxidation kinetics and resulting oxide microstructures were sensitive to impurities in the matrix. Activation energies for oxidation ranged from 28 kcal/mol for Si to 122 kcal/mol for hot-pressed Si_3N_4.

538. **Valori, R., "Rolling Contact Fatigue Endurance of Silicon Nitride", Naval Air Propulsion Test Center, Trenton, New Jersey, Research Report No. NAPTC-PE-42 (August 1974). (AD 785 854)**

Rolling contact fatigue studies compared hot-pressed Si_3N_4 with M-50 steel. Si_3N_4 was superior by at least an order of magnitude. Surface finish affects fatigue life of Si_3N_4 and skidding may degrade its surface durability.

539. **Van Wyk, J. W., "Ceramic Airframe Bearings", Boeing Aerospace Company, Seattle, Washington, Naval Air Systems Command Contract Report No. D180-17996-1 (February 1974). (AD 779 050)**

Ceramic-solid-lubricant material test program was conducted to select materials and lubricants for a plain spherical bearing design. Best performance, at stress levels to 7500 psi, was obtained with an Al_2O_3 rider sliding against a Si_3N_4 plate lubricated with MoS_2.

540. **Van Wyk, J. W., "Ceramic Airframe Bearings", Boeing Aerospace Company, Seattle, Washington, Naval Air Systems Command Contract Report No. D180-19181-1 (November 1975). (AD-A020 170)**

A friction and wear screening program was conducted using Si_3N_4 rider specimens in contact with various ceramic coatings on Ti. Test results indicated that the ceramic airframe bearing shows promise for future application, but that additional development was required.

541. **Van Wyk, J. W., "Ceramic Airframe Bearings", Boeing Aerospace Company, Seattle, Washington, Naval Air Systems Command Contract Report No. D180-19447-1 (February 1976). (AD-A025 142)**

A friction and wear screening investigation of ceramic coatings, lubricants, and lubricant reservoir designs were conducted for an 1100 F bearing application. An improved lubricant reservoir ceramic bearing design was developed using a hot-pressed Si_3N_4 ball sliding against an Al_2O_3 coating on Ti.

542. **Vasilos, T., and Cannon, R. M., Jr., "Improving the Toughness of Refractory Compounds", Avco Corporation, Lowell, Massachusetts, National Aeronautics and Space Administration Contract Report No. NASA–CR–134813 (November 1975). (N76-20230)**

Charpy impact testing at 2415 F established the effectiveness of higher purity Si_3N_4 powder sources in reducing the scatter measurements and in improving the short-time bend strengths as well as bend stress rupture properties. Additions of stabilized ZrO_2 enhanced the low and high temperature bend strengths for all grades of Si_3N_4 powder.

543. **Vincenzini, P., "Hot Pressing of Silicon Nitride: Analysis of Densification Mechanisms", Scientific Translation Service, Santa Barbara, California, National Aeronautics and Space Administration Contract Report No. NASA-TT-F-17132 (August 1976). Translation of Ceramurgia, 5 (1975), pp 184-188. (N76-28371)**

The problems involved in the hot pressing of Si_3N_4 are reviewed with special reference to the manufacturing technique and to the thermodynamic and kinetic aspects of the sintering process. Probable mechanisms of densification and the effect of additives and impurities on the process are discussed. Areas of future research are suggested.

544. **Wahl, N. E., "Development and Characterization of Materials Resistant to Supersonic Erosion", Textron's Bell Aerospace Company, Buffalo, New York, Air Force Materials Laboratory Contract Report No. AFML-TR-74-139 (May 1974). (AD-B000 124L)**

Hot-pressed Si_3N_4 and BN were two of the materials evaluated for rain erosion resistance. The Si_3N_4 exhibited no erosion for expanded periods of time at supersonic speeds.

545. **Wells, W. K., "Silicon Nitride as a High-Temperature Radome Material", University of California, Lawrence Radiation Laboratory, Livermore, U. S. Atomic Energy Commission Contract Report No. UCRL-7795 (May 1964).**

Si_3N_4 was investigated for applications in structural elements in high-temperature, air-cooled reactors. Thermal stress parameters and high temperature (at least 2700 F) strength of Si_3N_4 were superior to those of alumina and beryllia. Of the properties of Si_3N_4 that are significant for radome applications, the electrical properties are least known.

546. **Wheildon, W. M., Baumgartner, H. R., Sundberg, D. V., and Torti, M. L., "Ceramic Materials in Rolling Contact Bearings", Final Report 3 January 1972-3 February 1973, Norton Company, Worcester, Massachusetts, Naval Air Systems Command Contract Report (February 1973). (AD 761 200)**

Screen rolling contact fatigue tests were conducted on high strength Si_3N_4, SiC, and Al_2O_3. Si_3N_4 with conventional lubricants showed excellent life, greater than M-50 steel, at comparable loads. Friction and wear properties were nearly the same for steel-steel and steel-Si_3N_4 combinations.

547. **Wright, T. R., and Niesz, D. E., "Improved Toughness of Refractory Compounds", Battelle's Columbus Laboratories, Columbus, Ohio, National Aeronautics and Space Administration Contract Report No. NASA-CR-134690 (October 1974). (N74-34069)**

Attempt to remove SiO_2 from Si_3N_4 powder by thermal treatment and compensating remaining O with Mg and Al nitride additives. Mg nitride aided densification while Al_2O_3 had to be added to the AlN composition to densify it. Materials hot pressed from these compositions showed no improvement in impact strength compared to existing materials, but their high temperature mechanical properties were improved.

548. **Wuensch, B. J., and Vasilos, T., "Self-Diffusion in Silicon Nitride", Interim Report 1 January 1973-21 December 1973, Avco Corporation, Systems Division, Lowell, Massachusetts, Office of Naval Research Contract Report (April 1974). (AD 779 901)**

Stable isotopes Si^{29} and N^{15} will be used as tracers to simultaneously obtain self-diffusion coefficients in Si_3N_4 materials including α-Si_3N_4, β-Si_3N_4, "sialons", etc.

549. **Wuensch, B. J., and Vasilos, T., "Self-Diffusion in Silicon Nitride", Avco Corporation, Systems Division, Lowell, Massachusetts, Office of Naval Research Contract Report (1975). (AD-A021 175)**

Program to develop techniques for simultaneous measurement of Si and N self-diffusion in Si_3N_4. Both α- and β-Si_3N_4 and a variety of "sialons" were examined and characterized. Specimens selected for measurement were a dense high purity α- and a dense commercial grade β-Si_3N_4.

550. **Yamawaki, M., and Hoch, M., "Vaporization of Silicon Nitride", Final Report, 1 January 1972-31 December 1972, University of Cincinnati, Ohio, Air Force Materials Laboratory Contract Report No. AFML-TR-73-240 (October 1973). (AD 773 333)**

The vaporization of Si_3N_4 was studied to determine the gaseous products and the composition of the remaining phase. The gas phase above Si_3N_4 consisted mainly of N, but Si (at mass 28) was also detected. It was found that the Si_3N_4/Si ratio did not change after a certain time, apparently due to the formation of a constant boiling composition that could be $S_{.52}N_{.48}$.

551. **Yeh, H. C., Sanders, W. A., and Fiyalko, J. L., "Silicon Nitride - Aluminum Oxide Solid Solution (SiAlON) Formation and Densification by Pressure Sintering", National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio, Report No. NASA-TM-X-3299 (October 1975). (N76-10317)**

Stirred-ball-mill-blended Si_3N_4 and Al_2O_3 powders were pressure sintered to investigate the mechanism of solid solution formation and densification in the Si_3N_4-Al_2O_3 system. The compaction behavior of the powdered blends during pressure sintering was determined by observing the density of the powder compact as a function of time and temperature.

552. **Forgeng, W. D., and Gerby, R. W., "Silicon-Oxygen-Nitrogen Crystalline Refractory Powder", U. S. Patent 2,968,530 (January 17, 1961), assigned to Union Carbide Corporation.**

Describes methods of obtaining powder of approximate composition Si_2ON. These include heating Si in O-N gas mixture, nitriding Na silicate or H_3BO_3 bonded Si pellets, heating Si_3N_4 in O, etc.

553. **Dess, H. M., "Method of Making Foamed Silicon Nitride", U. S. Patent 3,084,998 (April 9, 1963), assigned to Union Carbide Corporation.**

Method of producing porous Si_3N_4 comprising of mixing finely divided Si having an oxidic silicon film with aqueous HF insufficient to dissolve all of the Si, to form a stable foam which is dried and heated in a N atmosphere at 1100-1500 C to convert it to Si_3N_4.

554. **Parr, N. L., and Martin, G. F., "Heat Resisting Material and Method for Producing It", U. S. Patent 3,222,438 (December 7, 1965), assigned to the National Research Development Corporation.**

A method of making a shaped body designed to withstand high temperatures and to resist creep and thermal shock at such temperatures. A powdered mixture consisting of Si and 5-10% by weight of finely divided SiC, particle size 400 B.S., evenly distributed in the Si is compacted into the required shape. Mixture is fired in an atmosphere of N initially at a temperature below the melting point of Si for a sufficient time to produce a rigid network of Si_3N_4. Shape is then fired at a temperature above the melting point of Si to complete the nitriding of the remaining uncombined Si.

555. **Johnson, R. C., Alley, J. K., Warwick, W. H., and Shell, H. R., "Synthesis of Fibrous Silicon Nitride", U. S. Patent 3,244,480 (April 5, 1966), assigned to the United States of America as represented by the Secretary of the Interior.**

A method of producing Si_3N_4 fibers by reacting at an elevated temperature (about 1400 C) gaseous N with a silica material and a reducing agent, consisting of graphite or lampblack.

556. **Washburn, M. E., "Production of Silicon Oxynitride", U. S. Patent 3,356,513 (December 5, 1967), assigned to the Norton Company.**

Si_2ON_2 is produced by heating a mixture of silica and Si in a controlled, N and O containing, atmosphere with an alkaline earth oxide as a promoter, in the amount up to 5% by weight. The reactant mixture may be molded to shape and then fired, or loose reacted powder may be hot pressed to make refractory bodies having a high degree of chemical and thermal stability.

557. **Parr, N. L., and Martin, G. F., "Method of Glazing Silicon Nitride Shaped Body and Article", U. S. Patent 3,394,026 (July 23, 1968), assigned to the National Research Development Corporation.**

Glaze comprising 5 w/o Al_2O_3, 93 w/o SiO_2, and 2 w/o Fe_2O_3 is fired at 1300-1500 C in O.

558. **Evans, C. C., "Manufacture of Silicon Nitride", U. S. Patent 3,394,991 (July 30, 1968), assigned to the Ministry of Technology in the Government of the United Kingdom.**

High yields of Si_3N_4 whiskers, having high tensile strength and substantially uncontaminated by other crystalline phases, are produced by heating Si/SiO_2 mixture to form a Si-containing vapor, reacting this vapor with N at about 1400 C in the presence of C and H, whereby Si_3N_4 whiskers are deposited on substrates adjacent to the gaseous reaction zone.

559. **Krock, R. H., and Kelsey, R. H., "Preparation of Silicon Nitride Whiskers", U. S. Patent 3,413,090 (November 26, 1968), assigned to P. R. Mallory and Company, Inc.**

A vapor phase deposition method for producing α-Si_3N_4 whiskers comprising the reaction of Si in alumina or refractory boats with N-Ar mixtures at temperatures between 1350 and 1600 C.

560. **Deeley, G. G., and Herbert, J. M., "Silicon Nitride", U. S. Patent 3,455,729 (July 15, 1969), assigned to The Plessey Company.**

Method of reducing the tendency of Si_3N_4 bodies to fracture when subjected to thermal shocks by exposing them to Li_2O vapor for 3-200 hours at 500-1500 C.

561. **Lubatti, E., Pappalardo, S., and Mirarchi,U., "Process for Preparing Manufactured Articles of Silicon Nitride, Also in Admixture with Silicon Carbide", U. S. Patent 3,468,992 (September 23, 1969), assigned to Montecatini Edison, S.p.A.**

A process for preparing manufactured articles of Si_3N_4, comprising admixing Si_3N_4 powder of at least 90% purity and a fineness of less than 0.075 mm with less than 25% by weight of the mixture of a binder selected from the group consisting of boric acid, boric anhydride, and boron phosphate. The mixture is cold compacted under a pressure between 0.5 and 5 t/cm^2 and the resulting material is sintered in a N atmosphere selected from the group consisting of N, NH_3, and air at a temperature between 850 and 1250 C.

562. **Lumby, R. J., "Method of Manufacturing Silicon Nitride", U. S. Patent 3,591,337 (July 6, 1971), assigned to Joseph Lucas (Industries), Ltd.**

Si_3N_4 is manufactured by mixing finely divided Si with finely divided Si_3N_4 and then heating resultant mixture in a non-oxidizing atmosphere containing N. Normally, finely divided Si is used alone, but it was found that the addition of some Si_3N_4 leads to a reduction in operating time which is considerably greater than the reduction which would be expected because some of the mixture is already constituted by Si_3N_4.

563. **Taylor, R. A., "Method of Producing Silicon Nitride Articles", U. S. Patent 3,778,231 (December 11, 1973), assigned to Birmingham Small Arms Company, Ltd.**

Method of producing a Si_3N_4 article by forming a Si powder compact, sintering the compact in a N-free atmosphere, machining the Si compact to a required accuracy, and subsequently nitriding it in the temperature range from 1180-1450 C.

564. **Henney, J. W., and Jones, J.W.S., "Silicon Nitride Ceramics", U. S. Patent 3,811,928 (May 21, 1974), assigned to the United Kingdom Atomic Energy Authority.**

Si_3N_4 ceramics made by nitriding mixtures of Si and B or BN and oxidizing product by heating in air at 1050-1350 C to form glassy protective layer. For example, a 95:5 Si-B mixture is nitrided at temperatures up to 1450 C, ground and oxidized 2 hours at 1350 C to yield oxidation-resistant material. (Also issued as German Patent 2,152,066)

565. **May, E.R.W., "Production of Silicon Nitride Material Components", U. S. Patent 3,819,786 (June 25, 1974), assigned to the National Research Development Corporation.**

Method of forming Si_3N_4 components by hot milling and then shaping a dough-like material comprising Si powder and a suitable organic chemical binder consisting of 34-40% butyl methyl methacrylate and 60-65% trichloroethylene and subsequently subjecting the form to a nitriding treatment.

566. **Coe, R. F., "Silicon Nitride Composites", U. S. Patent 3,819, 787 (June 25, 1974), assigned to Joseph Lucas (Industries), Ltd.**

Si_3N_4 composites made by hot pressing a powdered mixture containing Si_3N_4 (>90% α-phase) and 1.25-5% MgO flux onto Si_3N_4. Two Si_3N_4 pieces were joined by spreading a layer of the mixture between them and hot pressing at 1650 C to give a bond with modulus of rupture 84 kg/mm^2. (Also issued as German Patent 2,135,648)

567. **Davidge, R. W., and Evans, A. G., "Improvements In or Relating to Silicon Nitride Artefacts", U. S. Patent 3,820,120 (June 25, 1974), assigned to the United Kingdom Atomic Energy Authority.**

Method of increasing the strength of a porous Si_3N_4 artifact by subjecting it to controlled oxidation in air at 1000 C. Room temperature strength is increased from 220 to 280 MN m^{-2}. (Also issued as British Patent 1,312,688)

568. **Layden, G. K., "Densification of Silicon Nitride", U. S. Patent 3,821,005 (June 28, 1974), assigned to the United Aircraft Corporation.**

High strength hot-pressed Si_3N_4 by use of $\sim$5 w/o phosphates, phosphides, arsenates, arsenides or nitrides of Al or Ga as sintering aids.

569. **Gazza, G. E., "Hot Pressed, High Strength Silicon Nitride", U. S. Patent 3,830,652 (August 20, 1974), assigned to the United States of America as represented by the Secretary of the Army.**

Fabrication of high strength, high density Si_3N_4 by adding 1.0-3.5 w/o yttrium compound [Y_2O_3, $Y(NO_3)_3$, YCl_3] to Si_3N_4 powder and pressing at 1750-1850 C and 6000-7000 psi pressure.

570. **Stokes, R. F., and Hunt, B. J., "Method of Joining a Pair of Silicon Nitride Parts", U. S. Patent 3,833,348 (September 3, 1974), assigned to Joseph Lucas (Industries), Ltd.**

Parts were joined by oxide glasses of compositions: (1) 63 w/o Mn oxide, 38 w/o SiO_2, and (2) 50 w/o Mn oxide, 39 w/o SiO_2, and 11 w/o Al_2O_3.

571. **Komeya, K., Tsuge, A., Inoue, H., and Murata, H., "Heat Resistant and Strengthened Composite Materials and Method for Producing Same", U. S. Patent 3,833,389 (September 3, 1974), assigned to Tokyo Shibaura Electric Company, Ltd.**

Combination of AlN and/or Si_3N_4 with powders of an oxide of La, Ce, Sc, Y, and/or YAG and with powders or whiskers of SiC, BN, and/or C were mixed and sintered to obtain heat resistant and strengthened composite materials.

572. **Coe, R. F., and Lumby, R. J., "Silicon Nitride Products", U. S. Patent 3,835,211 (September 10, 1974), assigned to Joseph Lucas (Industries), Ltd.**

A method of manufacturing a composite in which Si_3N_4 powder is mixed with C fibers coated with a layer of SiC (0.1-2.0 μm thick) to prevent reaction between the fibers and Si_3N_4 and a layer of Si_3N_4 (1 μm thick) to aid bonding of the fibers to the Si_3N_4 matrix and mixture is then hot pressed. The composites have good cross-breaking strength. (Also issued as British Patent 1,305,910)

573. **Richerson, D. W., and Washburn, M. E., "Hot Pressed Silicon Nitride", U. S. Patent 3,836,374 (September 17, 1974), assigned to the Norton Company.**

Method of producing a Si_3N_4 product containing a complex metal silicate having the general formula $Ro \cdot Al_2O_3 \cdot SiO_2$ (Ro being the metal oxide). The flexural strength at 20 C is >100,000 psi and at 1375 C is >45,000 psi and the density between 3.1 and 3.3 g/cc.

574. **Arrol, W. J., "Method of Manufacturing Silicon Nitride Products", U. S. Patent 3,839,540 (October 1, 1974), assigned to Joseph Lucas (Industries), Ltd.**

Compacts containing MgO or Mg silicate fluxes and binders are nitrided at 1200 C in 90 v/o N-10 v/o H to give α-Si_3N_4 of density 2.1 g/cm^3. Resulting compacts are hot pressed to final density of 3.2 g/cm^3 in graphite dies at 1750 C. (Also issued as British Patent 1,340,696)

575. **Lumby, R. J., Grieveson, P., and Stokes, R. F., "Silicon Nitride Products", U. S. Patent 3,839,541 (October 1, 1974), assigned to Joseph Lucas (Industries), Ltd.**

Method of manufacturing Si_3N_4 compacts, $\geqslant$80% α-phase from powdered Si (~10 μ grain size) containing 1.4-2.5% reactive O and 5% α-Si_3N_4. (Also issued as British Patent 2,132,152 and German Patent 2,147,513)

576. **Ezis, A., Goodyear, M. U., and Styhr, K. H., "Method of Making a Bonded Silicon Nitride Article Having Portions of Different Density", U. S. Patent 3,854,189 (December 17, 1974), assigned to the Ford Motor Company.**

Method of forming a complex article as a rotor for a gas turbine engine in which the best characteristics of hot-pressed Si_3N_4 and slip-case Si_3N_4 materials are brought together. The structure is bonded together by a strong and uniform bond at the junction between the different materials.

577. **Washburn, M. E., "Control System in an Apparatus for Reacting Silicon With Nitrogen", U. S. Patent 3,854,882 (December 17, 1974), assigned to the Norton Company.**

Si_3N_4 is proposed by an exothermic reaction in which powdered Si is spread on trays in a closed, electrically heated reaction chamber fed with N, Ar, and NH_3. The flow rate of N is governed by the pressure in the chamber and is used as a means for controlling the operation. The periodic on and off cycling of the Ar provides high yields of Si_3N_4 and prevents runaway reaction rates.

578. **Cutler, I. B., "Production of Silicon Nitride from Rice Hulls", U. S. Patent 3,855,395 (December 17, 1974), assigned to the University of Utah.**

Method of producing Si_3N_4 from the reaction of rice hulls and N, either singly or in combination with a catalyst comprising Fe, at 1100-1350 C.

579. **Stokes, R. F., and Hunt, B. J., "Method of Joining a Pair of Silicon Nitride Parts", U. S. Patent 3,881,904 (May 6, 1975), assigned to Joseph Lucas (Industries), Ltd.**

Method of forming a glass joint between Si_3N_4 parts by inserting a powdered glass (30-60 w/o SiO_2, 11-57 w/o MgO, and up to 32 w/o Al_2O_3) between the parts and heating the pressed parts in an inert atmosphere. (Also issued as British Patent 1,374,817)

580. **Chaundy, G. J., Ezis, A., Goodyear, M. U., Howes, B. T., Johnson, C. F., and Styhr, K. H., "Method of Making a Bonded Silicon Nitride Article Having Portions of Different Density", U. S. Patent 3,885,294 (May 27, 1975), assigned to the Ford Motor Company.**

Method of forming a complex article as rotor for a gas turbine engine in which the best characteristics of hot-pressed Si_3N_4 and an injection molded Si_3N_4 material are brought together. The structure is bonded together by a strong and uniform bond at the junction between the different materials.

581. **Goodyear, M. U., Ezis, A., and Styhr, K. H., "Making a Triple Density Article of Silicon Nitride", U. S. Patent 3,887,411 (June 3, 1975), assigned to the Ford Motor Company.**

Method of preparing a triple density Si_3N_4 in which the first element is formed by hot pressing a mixture of 95-99.5 w/o Si_3N_4 particles and 0.5 to 5.0 w/o MgO; the second element is formed by injection molding Si metal particles and a thermoplastic resin carrier and subsequently burning out the carrier; the third element is formed slip casting in contact with the second element and then nitriding together.

582. **Styhr, K. H., Ezis, A., and Goodyear, M. U., "Method of Making a Triple Density Silicon Nitride Article", U. S. Patent 3,887,412 (June 3, 1975), assigned to the Ford Motor Company.**

Method of preparing a triple density Si_3N_4 in which the first element is formed by hot pressing a mixture of 95-99.5 w/o Si_3N_4 particles and 0.5 to 5.0 w/o MgO; the second element is formed by injection molding Si metal particles and a thermoplastic resin carrier and subsequently burning out the carrier; the third element is independently cast and sintered in an inert atmosphere, bonded to the second element with slip and then the second and third elements are nitrided together.

583. **Richerson, D. W., "Hot Pressing Silicon Nitride Containing Finely Dispersed Silicon Carbide or Silicon Aluminum Oxynitride", U. S. Patent 3,890,250 (June 17, 1975), assigned to the Norton Company.**

Method of producing a Si_3N_4 containing finely dispersed SiC or $SiAlON_2$ having high strength at room and elevated temperatures and controlled low electrical resistivity. The transverse rupture strength at 20 C is >100,000 psi as measured by a four-point test, and at 1375 C, >40,000 psi as measured by a three-point test.

584. **North, J. M., and Wilks, R. S., "Sintered Artifacts and the Like", U. S. Patent 3,891,735 (June 24, 1975), assigned to the United Kingdom Atomic Energy Authority.**

Method of preparing a Si_3N_4 article with a fine matrix of apetures by stacking intervening layers of composite plastics in preformed sheets made of a powder refractory and a thermosetting binder, as poly (vinyl butyral), which bond the sheets together at the ribs or walls of the preformed material. The stack is heated to cure the binder and burn off sheet material and then fired to form the sintered article.

585. **Holdsworth, M. R., "Method of Manufacturing Hot Pressed Ceramic Material Based on Silicon Nitride", U. S. Patent 3,892,835 (July 1, 1975), assigned to Joseph Lucas (Industries), Ltd.**

Method of preventing reaction between Si_3N_4 and graphite during hot pressing. The powder compact is coated with Al_2O_3 and the mold with BN. (Also issued as German Patent 2,316,348)

586. **Brennan, J. J., "Tantalum Wire Reinforced Silicon Nitride Articles and Method for Making the Same", U. S. Patent 3,900,626 (August 19, 1975), assigned to United Aircraft Corporation.**

Method of preparing an impact-resistant fiber-reinforced ceramic from a number of continuous Ta wires preferentially oriented and embedded in a hot-pressed Si_3N_4 matrix which approaches theoretical density.

587. **Kamigaito, O., and Oyama, Y., "Method for Producing Ceramics of Silicon Nitride", U. S. Patent 3,903,230 (September 2, 1975), assigned to Kabushiki Kaisha Toyota Chuo Kenkyusho, Japan.**

A method of producing heat-, oxidation-, and abrasion-resistant Si_3N_4 ceramics of low thermal expansion by hot pressing mextures containing Si_3N_4 10-80 m/o, Al_2O_3 10-90 m/o and optionally AlN 2-70 m/o at 1650-2000 C in a nonoxidizing atmosphere. (Also issued as German Patent 2,262,785)

588. **Torti, M. L., "Composite Ceramic Turbine Rotor", U. S. Patent 3,905,723 (September 16, 1975), assigned to the Norton Company.**

Turbine rotor comprising high-density (hot-pressed) hub and low-density (sintered) blades that may be fabricated from Si_3N_4.

589. **Torti, M. L., and Richerson, D. W., "High Strength Composite Ceramic Structure", U. S. Patent 3,911,188 (October 7, 1975), assigned to the Norton Company.**

A hot-pressed Si_3N_4 composite body with its outer layers locked in compressive stress is formed with surface layers of Si_3N_4 having a predetermined thermal expansion coefficient and an internal layer made up of a mixture of Si_3N_4 and SiC which has a thermal expansion coefficient less than that of the outer layer.

590. **Brennan, J. J., Novak, R. C., and DeCrescente, M. A., "Tungsten Wire Reinforced Silicon Nitride Articles and Method for Making the Same", U. S. Patent 3,914,500 (October 21, 1975), assigned to United Aircraft Corporation.**

Method of producing a ceramic article for use in gas turbine engine environment comprised of a matrix of hot-pressed Si_3N_4 with reinforcing filaments of W embedded in it.

591. **Mangels, J. A., "Improved Flowmolding Composition", U. S. Patent 3,926,656 (December 16, 1975), assigned to the Ford Motor Company.**

A method of preparing an improved flowmolding composition for molding Si powder shapes. The composition includes a granular material (65-77 v/o) and a deflocculant (0.1-1.0 v/o) and the remainder of volume being a 90/10 ratio by weight mixture of a 135 F melting paraffin wax and a 195 F microcrystalline wax.

592. **Lumby, R. J., "Manufacture of Silicon Nitride Powder", U. S. Patent 3,937,792 (February 10, 1976), assigned to Joseph Lucas (Industries), Ltd.**

Formation of high α-Si_3N_4 powder from Si powder by using various measures to control exothermic reaction and to avoid formation of β-Si_3N_4.

593. **Masaki, H., "Method of Producing a Sintered Silicon Nitride Base Ceramic and Said Ceramic", U. S. Patent 3,950,464 (April 13, 1976), assigned to Kabushiki Kaisha Toyota Chuo Kenkyusho, Japan.**

Method of forming a pressureless sintered Si_3N_4 based ceramic, having improved mechanical and chemical properties, by the addition of two metal oxides that form a spinel.

594. **Lange, F. F., "Fully Dense Ceramic Article Employing Magnesium Oxide as a Sintering Aid", U. S. Patent 3,953,221 (April 27, 1976), assigned to the United States of America as represented by the Department of the Navy.**

Method of preparing dense, thermal resistant Si_3N_4 ceramics by mixing Si_3N_4, Al_2O_3, and MgO and sintering in a N atmosphere under ambient pressure at 1400-1750 C.

595. **Henney, J. W., and Jones, J.W.S., "Conductivity of Silicon Nitride", U. S. Patent 3,956,193 (May 11, 1976), assigned to the United Kingdom Atomic Energy Authority.**

Method of improving the electrical conductivity of a Si_3N_4 body by heating at 1350-1550 C, high enough to partially decompose the Si_3N_4 but below Si evaporation temperature, in an atmosphere of Ar or H which is inert to Si. The Si_3N_4 material is used as a resistance heater. (Also issued as British Patent 1,397,070)

596. **Mazdiyasni, K. S., and Cooke, C. M., "Synthesis of High Purity, Alpha Phase Silicon Nitride Powder", U. S. Patent 3,959,446 (May 25, 1976), assigned to the United States of America as represented by the Department of the Air Force.**

Method of producing high purity α-Si_3N_4 powder by thermal decomposition of product of reaction of $SiCl_4$ with excess NH_3 gas in benzene or hexane at 0 C.

597. **Cutler, I. B., "Solid Solution of Aluminum Oxide in Silicon Nitride", U. S. Patent 3,960,581 (June 1, 1976), assigned to the University of Utah.**

Preparation of Si-Al-O-N compositions by sintering with C and N mixtures of clay, rice hulls, and Al source.

598. **Mangels, J. A., "Method of Increasing the Oxidation Resistance of Silicon Nitride", U. S. Patent No. 3,983,198 (September 28, 1976), assigned to the Ford Motor Company.**

The oxidation resistance of a Si_3N_4 article is increased by preheating to 2500-2750 F, inserting the Si_3N_4 article into the preheated furnace, and maintaining it in the furnace for a period sufficient to develop an oxidation resistant surface on the article.

599. **Mazdiyasni, K. S., "Method of Fabricating Silicon Nitride Bodies", U. S. Patent Application 452 038 (filed March 18, 1974), assigned to the United States of America as represented by the Department of the Air Force.**

Method of fabricating Si_3N_4 bodies by mixing Si_3N_4 powder with an oxide, hydride, or nitride of yttrium or an element of the lanthanide series and hot pressing for 30-60 minutes at 1600-1700 C.

600. **Jacobson, H. W., "Amorphous Silicon Nitride Compositions Containing Carbon and Vapor Phase Process", U. S. Patent Application B581,564 (March 23, 1976), assigned to E. I. du Pont de Nemours and Company.**

Method of preparing an amorphous Si_3N_4 composition from 95-99.9% amorphous Si_3N_4 and 0.1-5.0% C. Composition is useful in the preparation of dense sialon.

601. **McDonough, W. J., and Rice, R. W., "Ceramic Compositions", U. S. Patent Application 695,296 (June 11, 1976), assigned to the United States of America as represented by the Department of the Navy.**

Hot-pressed Si_3N_4 containing 1-25 w/o ZrC, ZrN, $ZrSiO_4$, or a mixture of these.

602. **"Ceramic Materials", Belgian Patent 823,935 (April 16, 1975), assigned to Joseph Lucas (Industries), Ltd.**

Hot-pressed Si-Al-O-N material formed from mixture of powdered Si_3N_4, AlN, Al_2O_3, and SiO_2.

603. **Parr, N. L., and Martin, G. F., "Improvements in or Relating to Shaped Silicon Nitride Bodies and Their Manufacture", British Patent 895,769 (May 9, 1962), assigned to the National Research Development Corporation.**

A method of making a shaped body of self-bonded Si_3N_4 designed to withstand high temperature and to resist creep and thermal shock. Powdered Si is compacted in a block which is fired in an atmosphere of N at a temperature below the melting point of Si for a period of at least one hour to produce a self-supporting, readily-machinable block. The block is worked to the required finished shape and the shaped body is fired in an atmosphere of N to effect complete nitriding of the Si.

604. **Parr, N. L., "An Improved Heat Resisting Material Comprising Self-Bonded Silicon Nitride with or without Silicon Carbide Dispersed Therein and Method for Producing It", British Patent 942,082 (November 20, 1963), assigned to the National Research Development Corporation.**

A method of making a shaped body designed to withstand high temperatures and to resist creep and thermal shock at such temperatures consisting of a self-bonded Si_3N_4. Powdered silicon is compacted in the required shape and fired in an atmosphere of N initially between 1250 and 1350 C for a sufficient time to produce partial nitriding. Nitriding is completed by continuing the firing in N at 1700 C to produce a material high in β-Si_3N_4.

605. **Deeley, G. G., "Improvements in or Relating to Refractory Bodies", British Patent 947,576 (January 22, 1964), assigned to The Plessey Company, Ltd.**

Method of forming a refractory body of Si_3N_4 fibers and a continuous polycrystalline phase by first forming fibers by a reaction between Si vapor and NH_3 at temperatures between 1300 and 1500 C. Nitride fibers produced are mixed with chromium carbide, B, and Si and heated to a temperature at which the constituents form a polycrystalline mixture of chromium boride, silicon carbide, and Si_3N_4 fibers.

606. **Deeley, G. G., "Method of Producing High Density Silicon Nitride", British Patent 970,639 (September 23, 1964), assigned to The Plessey Company, Ltd.**

A method of forming a Si_3N_4 ceramic including the step of mixing 0.1% to 25% by weight of a fluxing agent in powder form with powdered Si_3N_4 and then pressure sintering the mixture to convert the Si_3N_4 into a ceramic form.

607. **Evans, C. C., "Production of Silicon Nitride Whiskers", British Patent 998,167 (July 14, 1965), assigned to T. I. (Group Services), Ltd.**

A method of producing whiskers of Si_3N_4 comprising heating Si powder to produce Si vapor and mixing this vapor with a stream of N gas in such a manner that the resultant reaction to produce whiskers of Si_3N_4 occurs in a zone displaced from the Si from which the vapor is produced.

608. **Coe, R. F., "Silicon Nitride Products", British Patent 1,092,637 (November 29, 1967), assigned to Joseph Lucas (Industries), Ltd.**

A method of making a Si_3N_4 product, comprising heating in a non-oxidizing atmosphere containing N and H (5-25% by volume) a quantity of powdered Si to a temperature not exceeding 1300 C so as to form powdered α-Si_3N_4, mixing the Si_3N_4 thus formed with MgO and $MgCO_3$, and subsequently pressing the resultant mixture to a predetermined shape at a temperature not exceeding 1650 C to produce a solid body.

609. **Parr, N. L., and Brown, R. L., "Spray Deposition of Silicon Powder Structures", British Patent 1,138,284 (December 27, 1968), assigned to National Research Development Corporation.**

Si powder flame-sprayed onto a preheated metal form coated with H_2O soluble release agent such as NaCl. After light machining the shaped compact is removed from the form and treated with N or NH_3 at high temperature to convert it to Si_3N_4.

610. **Taylor, R. A., "Improvements in or Relating to the Production of Silicon Nitride Articles", British Patent 1,168,499 (October 29, 1969), assigned to the Birmingham Small Arms Company, Ltd.**

A process for producing Si_3N_4 articles wherein a compact of Si powder is first sintered at temperatures between 800 and 1400 C in a protective atmosphere free from N and subsequently nitrided at 1350 C for 16 hours and at 1450 C for 20 hours.

611. **Parr, N. L., May, E.R.W., Godfrey, D. J., Lindley, M. W., and Brown, R. L., "Method of Production of Reaction Bonded Silicon Nitride Ceramic Matrix Composite Materials", British Patent 1,198,906 (July 15, 1970), assigned to the National Research Development Corporation.**

A method of production of reaction-bonded Si_3N_4 ceramic matrix composite materials comprising depositing Si powder by flame-spray means onto a reinforcement material which is in the form of a fiber or fibers and heating the matrix in a nitriding atmosphere to convert Si to Si_3N_4.

612. **Lumby, R. J., "Method of Manufacturing Silicon Nitride Powder", British Patent 1,206,468 (September 23, 1970), assigned to Joseph Lucas (Industries). Ltd.**

A method of manufacturing Si_3N_4 powder comprising mixing Si powder with Si_3N_4 powder and then heating the resultant mixture in a non-oxidizing atmosphere containing N.

613. **Surrall, A. J., "Silicon Nitride Sheet or Body", British Patent 1,238,551 (July 7, 1971), assigned to Leyland Gas Turbines, Ltd.**

Method of preparing disklike matrices of Si_3N_4 used in rotary regenerative heat exchangers from a homogeneous mixture of Si powder, a binder (vinyl butyral), and a plasticizer (debutyl phthalate) shaped and cured at 300-400 C before nitriding at 1350-1450 C in N. For shaping, corrugated and uncorrugated sheet of mixture is wound spirally into shape of the matrix.

614. **Lumby, R. J., and Maybury, J., "Silicon Nitride Products", British Patent 1,245,392 (September 8, 1971), assigned to Joseph Lucas (Industries), Ltd.**

Method of manufacturing Si_3N_4 product with improved strength at high temperature by mixing Si_3N_4 powder with a <10 w/o flux of Zn or Zn compound, grinding the mixture to 1 μm particle size and pressure sintering the mixture at 1740 C and 4000 psi in graphite dies.

615. **Deeley, G. G., "Nitriding Silicon", British Patent 1,273,145 (May 3, 1972), assigned to The Plessey Company, Ltd.**

α-Si_3N_4 is produced by the reaction of Si with N at 1180-1500 C in the presence of O(0.3-1.8 w/o of Si) and an inert gas such as Ar. A dispersant (0.1-50 w/o) such as Al_2O_3, MgO or Si_3N_4 may be mixed with the Si powder. Mixture is heated to 1180 C in N-Ar, then air is admitted and the temperature raised to 1195 C during 1 hour. Mixture is then heated in N-Ar while the temperature is raised at 15 C/hour Si is converted to Si_3N_4.

616. **Rose, K., and Ghosh, R. K., "Heat Resisting Materials Based on Silicon Nitride", British Patent 1,277,574 (June 14, 1972), assigned to Doulton and Company, Ltd.**

Method of forming Si_3N_4 consisting of compressing a mixture of 1-70% fugitive binder, 1-65% china and/or ball clay (or 1-63% mullite) and Si powder sufficient to yield predominately Si_3N_4 after nitriding. The clay components do not interfere with the final properties of the Si_3N_4 material.

617. **Arrol, W. J., "Silicon Nitride Product Preparation", British Patent 1,280,459 (July 5, 1972), assigned to Joseph Lucas (Industries), Ltd.**

Method of preparing a Si_3N_4 product comprising flame spraying Si and spraying inert fibrous material, such as asbestos, onto a mandrel, and then heating the Si and fibrous material in a N atmosphere.

618. **British Patent 1,305,910 (February 7, 1973). (See U. S. Patent 3,835,211, Entry No. 572)**

A method of manufacturing a composite in which Si_3N_4 powder is mixed with C fibers coated with a layer of SiC (0.1-2.0 μm thick) to prevent reaction between the fibers and Si_3N_4 and a layer of Si_3N_4 (1 μm thick) to aid bonding of the fibers to the Si_3N_4 matrix and mixture is then hot pressed. The composites have good cross-breaking strength.

619. **Arrol, W. J., "Silicon Nitride Products", British Patent 1,306,078 (February 7, 1973), assigned to Joseph Lucas (Industries), Ltd.**

A method of manufacturing a Si_3N_4 - C fiber composite similar to that described by Coe and Lumby in British Patent 1,305,910 (February 7, 1973).

620. **Parr, N. L., "Silicon Nitride Gas Bearings", British Patent 1,310,274 (March 14, 1973), assigned to the National Research Development Corporation.**

A bearing for shafts and like rotatable members in which the bearing surface is formed by a Si_3N_4 collar which is divided into a number of spaced segments and which is self-sustaining until self-generated gas pressures are produced.

621. **Heap, H. R., and Riley, C. C., "Method of Brazing", British Patent 1,310,997 (March 21, 1973), assigned to The English Electric Company, Ltd.**

Method of producing bodies of dense or porous self-bonded Si_3N_4 containing free Si are brazed using an alloy of Si (Cr or Ti) >5 a/o % Si, having thermal expansion characteristics substantially matching those of Si_3N_4.

622. **Komeya, K., and Inoue, H., "A Method of Manufacturing Heat-Resistant Reinforced Composite Materials", British Patent 1,312,315 (April 4, 1973), assigned to Tokyo Shibaura Electric Company, Ltd.**

Method of forming composite material comprising sintering mixtures of at least 85% of first component which is Al_4C_3, SiC, Si_3N_4, B_4C, or BN with oxides of Group IIIa or oxides of the lanthanide series. Examples of oxides used are Sc_2O_3, Y_2O_3, La_2O_3, or Ce_2O_3. Flexural strengths as high as 42.1 kg/mm^2 were obtained by sintering Si_3N_4-Si-Y_2O_3 mixtures in N.

623. **Parr, N. L., "Anchoring Ceramic Components", British Patent 1,312,339 (April 4, 1973), assigned to the National Research Development Corporation.**

Method of anchoring Si_3N_4 gas turbine blades to a metal member by inserting a part of the metal spindle into a cavity formed in Si_3N_4 blade and inductively heating to cause deformation of the metal within the cavity to prevent its withdrawal.

624. **British Patent 1,312,688 (April 4, 1973). (See U. S. Patent 3,820,120, Entry No. 567)**

625. **Lumby, R. J., "Manufacture of Silicon Nitride Powder", British Patent 1,314,170 (April 18, 1973), assigned to Joseph Lucas (Industries), Ltd.**

Manufacture of α-Si_3N_4 powder by careful control of nitriding temperature. Another claim deals with nitriding mixture of Si_3N_4 and Si powders.

626. **"Process for Producing a Mixture of Silicon Oxynitride and Silicon Carbide", British Patent 1,317,011 (May 16, 1973), assigned to Danfoss A/S.**

Process for producing a composition containing SiC and Si_2ON_2 free of SiO_2 by heating Si in a CO-N atmosphere with an O partial pressure of $<10^{-16}$ atmospheres at 1200-1600 C.

627. **Dell, R. M., and Walter, A. J., "Improvements In or Relating to Silicon Nitride", British Patent 1,326,730 (August 15, 1973), assigned to the United Kingdom Atomic Energy Authority.**

Protective Al_2O_3 coatings on Si_3N_4 formed by the decomposition of surface coating [preferably $Al(NO_3)_3$] or by CVD of $AlCl_3$ followed by hydrolysis.

628. **Brennan, A. C., and Phillips, J.G.R., "A Method of Manufacturing a Silicon Nitride Body", British Patent 1,335,842 (October 31, 1973), assigned to Joseph Lucas (Industries), Ltd.**

Method of producing Si_3N_4 tape, etc., by forming Si powder preform with polymer.

629. **Parr, N. L., "Silicon Nitride Bearings", British Patent 1,338,317 (November 21, 1973), assigned to the National Reserach Development Corporation.**

Designs for Si_3N_4 bearings for rotating shafts.

630. **Coe, R. F., "A Method of Producing a Pair of Interconnected Silicon Nitride Parts", British Patent 1,339,541 (December 5, 1973), assigned to Joseph Lucas (Industries), Ltd.**

Method of producing a pair of interconnected Si_3N_4 parts by applying a mixture of α-Si_3N_4 and 1-5 w/o MgO and hot pressing at 1400-1750 C.

631. **British Patent 1,340,696 (December 12, 1973). (See U. S. Patent 3,839,540, Entry No. 574)**

632. **"Watch Case", British Patent 1,340,711 (December 12, 1973), assigned to Kabushiki Kaisha Suwa Seikosha.**

Watch case comprising various hard materials including dense Si_3N_4.

633. **Cockbain, A. G., and Latimer, M. J., "The Manufacture of Articles Containing Silicon Nitride", British Patent 1,341,233 (December 19, 1973), assigned to The Plessey Company, Ltd.**

Hot molding of hot-pressed Si_3N_4 using graphite or vitreous carbon dies with or without BN coating as a release agent.

634. **"Method for the Production of Silicon Oxynitride Articles", British Patent 1,349,664 (April 10, 1974), assigned to the Norton Company.**

Method of producing shaped bodies of Si_2ON_2 by firing, in a N atmosphere, a preshaped mixture of Si and SiO_2, a portion of the latter comprising colloidal silica powder of particle size $\leqslant 0.5\ \mu$.

635. **Bird, J. R., and Tuitt, D. A., "Protective Silicon Nitride Coatings for Gas Turbine Engine Compressor Blades", British Patent 1,351,466 (May 1, 1974), assigned to the United Kingdom Secretary of State for Defence.**

Coating formed by plasma arc depositing Si into a compressor blade-shaped former coated with NaCl release agent, removing and nitriding the Si layer, and attaching the Si_3N_4 sheath formed to the blade by adhesive.

636. **British Patent 1,352,152 (May 8, 1974). (See U. S. Patent 3,839,541, Entry No. 575)**

637. **"Method of the Production of Silicon Oxynitride", British Patent 1,352,357 (May 8, 1974), assigned to the Norton Company.**

Production of Si_2ON_2 by nitridation of mixtures of Si and SiO_2. Control of exothermic reaction is critical.

638. **Bird, J. R., Gresham, H. E., Tuitt, D. A., and Bell, J., "Forming Silicon Nitride", British Patent 1,352,503 (May 8, 1974), assigned to the United Kingdom Secretary of State for Defence.**

Si is plasma arc sprayed onto former coated with NaCl to form both flat and corrugated sheets. Sheets are stacked and nitrided to form heat exchanger.

639. **Bird, J. R., "Method of Forming Ceramic Articles and Articles Formed by Such a Method", British Patent 1,352,853 (May 15, 1974), assigned to the United Kingdom Secretary of State for Defence.**

Method of forming shapes, e.g., turbine wheels, by sequentially hot pressing individual segments.

640. **McQuillan, A. D., and Caws, R. B., "Silicon Nitride Compounds and Method of Making Them", British Patent 1,357,046 (June 19, 1974), assigned to Advanced Materials Engineering, Ltd.**

A method of making Li-Si_3N_4 composition by reacting Si_3N_4 with Li either in vapor or molten form in an atmosphere free of O and N. An inert gas atmosphere as Ar may be used.

641. **Smith, D. W., Arrol, W. J., and Brennan, A. C., "A Method of Manufacturing Silicon Nitride Products", British Patent 1,357,099 (June 19, 1974), assigned to Joseph Lucas (Industries), Ltd.**

Method of preparing Si_3N_4 products as turbine blades and propellers in which Si_3N_4 powders and 1% MgO flux were ground, passed through a sieve of 400 BS, and mixed with an aqueous binder, containing 2% methyl cellulose, to give a paste containing 23.5% H_2O. Paste was pressed at 2.46 kg/mm^2 to the shape of a propeller and hot pressed 30 minutes at 2.11 kg/mm^2 at 1700 C to a density of 3.2 g/cm^3. (Also issued as German Patent 2,156,592)

642. **Korotkevich, M. N., Vulikh, A. I., Kutolin, R., and Kutolin, S. A., "A Method of Preparing Nitrides, Oxides or Oxynitrides of Refractory Metals and Solid Solutions of Said Compounds", British Patent 1,357,418 (June 19, 1974).**

Preparation of compounds by electric-arc evaporation of metals or alloys into reactive gas comprising N, O, or other mixtures.

643. **Bird, J. R., "Method and Apparatus for Manufacturing Bladed Members from Powder Material", British Patent 1,359,896 (July 17, 1974), assigned to Rolls-Royce Limited.**

Method of manufacturing a turbine guide vane by hot pressing Si_3N_4-MgO mixtures. (Also issued as German Patent 2,302,202)

644. **Bird, J. R., "Improvements In or Relating to Hot Pressing Silicon Nitride", British Patent 1,364,451 (August 21, 1974), assigned to the United Kingdom Secretary of State for Defence.**

Method of forming several articles simultaneously in one mold.

645. **"Heat Resistive and Reinforced Composite Material Based on Trisilicon Tetranitride", British Patent 1,365,126 (August 29, 1974), assigned to Tokyo Shibaura Electric Company, Ltd.**

A heat-resistant and strengthened composite material is formed by molding a finely powdered Si_3N_4, an oxide of Y, Sc, La, or Ce, and Al_2O_3 together with a volatile binding material into a shaped mass and sintering or hot pressing in a nonoxidizing atmosphere at 1400-1900 C.

646. **Bird, J. R., "Improvements In or Relating to Forming Articles from Powder", British Patent 1,367,462 (September 18, 1974), assigned to the United Kingdom Secretary of State for Defence.**

Method of preparing Si_3N_4 articles requiring a minimum of machining by hot pressing spaced charges of Si_3N_4 powder and a fluxing agent to give a block of partially shaped articles with adjacent articles joined by a web. The remaining faces of each article are formed by a cutting tool which removes the webs.

647. **Bird, J. R., "Forming a Body from Silicon Nitride", British Patent 1,370,285 (October 16, 1974), assigned to the United Kingdom Secretary of State for Defence.**

Si_3N_3 powder with MgO added is hot pressed in a graphite mold with vaporizable cores of MgO + C + NH_4OH + flour at 1800 C and ~1100 psi pressure. The cores are vaporized and formed body is in the form of a heat exchanger matrix of Si_3N_4.

648. **Graham, R. P., Caws, R. B., Lawson, R. A., Colclough, R.T.G., and Mutsuddy, B., "Method of Making Hollow-Ware Articles from Powdered Material", British Patent 1,373,816 (November 13, 1974), assigned to Advanced Materials Engineering, Ltd.**

Method of making Si powder shapes for nitriding by blow molding, etc., a mixture of Si powder and plasticizer.

649. **British Patent 1,374,817 (November 20, 1974). (See U. S. Patent 3,881,904, Entry No. 579)**

650. **Hunt, B. J., and Stokes, R. F., "A Method of Joining a Pair of Silicon Nitride Parts", British Patent 1,375,358 (November 27, 1974), assigned to Joseph Lucas (Industries), Ltd.**

Method of forming a glass joint between Si_3N_4 parts by inserting a powdered glass containing Si and Mn oxides (30-60 w/o SiO_2, 11-57 w/o MnO and up to 32 w/o Al_2O_3) between the parts and heating the pressed parts in an inert atmosphere.

651. **North, J. M., "Improvements in or Relating to Shaped Plastic Artefacts", British Patent 1,375,855 (November 27, 1974), assigned to the United Kingdom Atomic Energy Authority.**

Method of molding shapes such as heat exchanger matrices using resin vehicle.

652. **Henney, J. W., and Jones, J.W.S., "Improvements in or Relating to Silicon Nitride Ceramics", British Patent 1,376,891 (December 11, 1974), assigned to the United Kingdom Atomic Energy Authority.**

Method of producing Si_3N_4 or Si_3N_4 and BN having protective coatings of fluxed borosilicate glass which comprise >1 w/o of the object and 1-20 w/o of B_2O_3.

653. **Prentice, T. C., "Improvements In or Relating to Matrix Structures", British Patent 1,377,153 (December 11, 1974), assigned to Advanced Materials Engineering, Ltd.**

Method of increasing strength of part by injecting powder/thermoplastic mixture into desired region.

654. **"Heat Resistant Composite Materials", British Patent 1,377,487 (December 18, 1974), assigned to Tokyo Shibaura Electric Company, Ltd.**

Hot-pressed materials comprising Si_3N_4 as one component, a second component consisting of at least one oxide of La, Ce, Sc, Y, and/or $Y_3Al_5O_{12}$, and a third component consisting of SiC and/or BN and/or C.

655. **Arrol, W. J., "Hot Pressed Silicon Nitride Products", British Patent 1,377,623 (December 18, 1974), assigned to Joseph Lucas (Industries), Ltd.**

Oxidation-resistant surface coatings applied on hot-pressed Si_3N_4 by heating, RF sputtering, or by vapor deposition.

656. **Bottoms, H. S., "Journal Bearings", British Patent 1,382,793 (February 5, 1975), assigned to Joseph Lucas (Industries), Ltd.**

High temperature journal bearing with Si_3N_4 elements.

657. **Sorrall, A. J., "Method of Brazing Ceramic Articles to One Another", British Patent 1,387,478 (March 19, 1975), assigned to British Leyland Truck and Bus Division Ltd.**

Joining porous Si_3N_4 pieces with braze obtained from decomposition of Mo salt, e.g., ammonium molybdate.

658. **Lines, D. J., "Ceramic Bearings", British Patent 1,389,410 (April 3, 1975), assigned to Joseph Lucas (Industries), Ltd.**

Bearing design with Si_3N_4 liner.

659. **"Method for Producing Ceramics of Silicon Nitride", British Patent 1,392,161 (April 30, 1975), assigned to Kabushiki Kaisha Toyota Chuo Kenkyusho, Japan.**

Hot-pressed materials comprising 10-80 m/o Si_3N_4 and 20-90 m/o Al_2O_3 or 10-80 Si_3N_4, 10-90 Al_2O_3 and <70 m/o AlN.

660. **Winter, G., Verbeek, W., and Mansmann, M., "Production of Shaped Articles of Silicon Carbide and Silicon Nitride", British Patent 1,392,685 (April 30, 1975), assigned to Bayer A.G.**

The process includes producing a silazine compound by reacting NH_3 with at least one C, containing halogeno-silane at up to 200 degrees. Solutions that are produced can be used to form fibers, thin films, etc., that are subsequently heated in N to form products comprising homogeneous mixtures of SiC and Si_3N_4.

661. **Parr, N. L., "Method of Producing High Density Silicon Nitride", British Patent 1,393,579 (May 7, 1975), assigned to the National Research Development Corporation.**

Hot pressing to high density of reaction-sintered Si_3N_4 infiltrated with MgO.

662. **Wilks, R. S., and Worrall, J., "Improvements In or Relating to the Manufacture of Artefacts", British Patent 1,396,773 (June 4, 1975), assigned to Advanced Materials Engineering, Ltd.**

Reaction-sintered Si_3N_4 heat-exchanger disks using a binder which minimizes oxide formation.

663. **Verbeek, W., "Production of Shaped Articles of Homogeneous Mixtures of Silicon Carbide and Nitride", British Patent 1,396,830 (June 4, 1975), assigned to Bayer A.G.**

Fibers, filaments, flakes, powders, films, coatings, and foams comprising SiC and Si_3N_4 are formed via silazane compounds that are decomposed to form moldable resins.

664. **"A Method for the Production of Mouldings of Great Hardness which Contains Silicon Nitride and/or Silicon Oxynitride", British Patent 1,396,916 (June 11, 1975), assigned to Annawerk GmbH.**

High hardness bodies of Si_3N_4 and/or Si_2ON_2 were prepared by reacting a silicon halide with an excess of NH_3, removing the ammonium halide by heating, mixing remaining powder with 5-8 w/o MgO, and hot pressing the mixture at 1300-1800 C.

665. **British Patent 1,397,070 (June 11, 1975). (See U. S. Patent 3,956,193, Entry No. 595)**

666. **Wilks, R. S., Prentice, T. C., Houlton, M. R., and Henney, J. W., "Improvements in or Relating to Refractory Artifacts", British Patent 1,403,273 (August 20, 1975), assigned to the United Kingdom Atomic Energy Authority.**

Si_3N_4 catalyst support bonded to refractory component by glass.

667. **Smith, D. W., "Method of Manufacturing Hot-Pressed Silicon Nitride Components", British Patent 1,405,171 (September 3, 1975), assigned to Joseph Lucas (Industries), Ltd.**

Method of making dense (3.2 g cm^{-3}) Si_3N_4 points for tools. (Also issued as German Patent 2,301,426)

668. **"Method for Producing a Sintered Silicon Nitride Base Ceramic and Said Ceramic Product", British Patent 1,406,571 (September 17, 1975), assigned to Kabushiki Kaisha Toyota Chuo Kenkyusho, Japan.**

Preparation of Si_3N_4-bare ceramics having high strength and good corrosion resistance by mixing 60-92 m/o finely powdered Si_3N_4 and metal oxides of MgO, ZnO, or NiO with Cr_2O_3, Y_2O_3, TiO_2, Al_2O_3, or SnO_2 and sintering in an inert atmosphere at 1600-1800 C for 2-3 hours.

669. **"High Density Silicon Nitride", British Patent 1,408,087 (October 1, 1975), assigned to the Norton Company.**

High-density, hot-pressed Si_3N_4 with Mg silicate second phase.

670. **Matkin, D. I., and Valentine, T. M., "Production of Refractory Material", British Patent 1,410,841 (October 22, 1975), assigned to Advanced Materials Engineering, Ltd.**

Si_3N_4 foam produced by nitriding Si foam. Latter powder is mixed with foamable resin to give preform.

671. **Henney, J. W., and Jones, J.W.S., "Improvements In or Relating to the Preparation of Silicon Nitride", British Patent 1,413,975 (November 12, 1975), assigned to the United Kingdom Atomic Energy Authority.**

Reaction-sintered Si_3N_4 made by nitriding Si-powder compact containing 1-5% B or B compound. Additive reduces exothermic-reaction effects and promotes uniform nitridation.

672. **Lumby, R. J., "A Method of Manufacturing Silicon Nitride Powder", British Patent 1,414,143 (November 19, 1975), assigned to Joseph Lucas (Industries), Ltd.**

High α-Si_3N_4 powder was prepared by heating a bed containing Si powder in N at a temperature low enough to prevent formation of β-Si_3N_4.

673. **Furlong, O. D., Moore, L., Matkin, D. I., and Cavell, I. W., "Fabrication Technique", British Patent 1,414,485 (November 19, 1975), assigned to Normalair-Garrett (Holdings), Ltd. and the United Kingdom Atomic Energy Authority.**

Shapes made by molding Si-epoxy resin mixture.

674. **Holdsworth, M. R., "A Method of Manufacturing Hot Pressed Ceramic Material Based on Silicon Nitride", British Patent 1,415,522 (November 26, 1975), assigned to Joseph Lucas (Industries), Ltd.**

Coating of Si_3N_4 preform with Al_2O_3 to minimize interaction with graphite die and to form product having dense surface layer of Si-Al oxynitride.

675. **Wilks, R. S., "Improvements In or Relating to Joining Silicon Nitride to Silicon Nitrides", British Patent 1,417,169 (December 10, 1975), assigned to the United Kingdom Atomic Energy Authority.**

Joining of Si_3N_4 pieces by nitriding Si layer between them.

676. **Henney, J. W., and Jones, J.W.S., "Improvements In or Relating to Preparation of Silicon Nitride", British Patent 1,417,690 (December 17, 1975), assigned to the United Kingdom Atomic Energy Authority.**

Group IIa metal is heated with Si to make preform which is nitrided. Additive increases rate of nitridation.

677. **"Catalytic Converter and Method of Making It", British Patent 1,426,216 (February 25, 1976), assigned to the Ford Motor Company, Ltd.**

Method of preparing a Si_3N_4-ceramic support for an automobile exhaust treatment catalyst having a high specified surface area and capable of being coated with a catalyst without an intermediate surface layer.

678. **Graham, R. P., Caws, R. B., and McQuillan, A. D., "Treatment of Permeable Refractory or Metal Materials", British Patent 1,432,559 (Aprill 22, 1976), assigned to Advanced Materials Engineering Ltd.**

Method of treating reaction-bonded Si_3N_4 with SiH_4 and NH_3 at >1000 C to produce Si_3N_4 in the body, thus improving physical and chemical properties.

679. **Cockbain, A. G., and John, W. H., "A Method of Producing Silicon Nitride Articles", British Patent 1,435,467 (May 12, 1976), assigned to The Plessey Company, Ltd.**

Si compact is coated with Si slurry, coating is partially nitrided and machined, and complete structure is nitrided to form precision part.

680. **Lumby, R. J., "Hot Pressed Ceramic Materials", Canadian Patent 941,141 (February 5, 1974), assigned to Joseph Lucas (Industries), Ltd.**

Method of manufacturing refractory ceramic products, particularly Si_3N_4 containing ~1% MgO by sintering in a die with simultaneous application of heat and pressure. As the temperature is increased, a pyrometric signal controls a hydraulic valve, so increased pressure is supplied. In the temperature range 750-1700 C, the pressure is 750-4000 psi.

681. **Smith, D. W., Arrol, W. J., and Brennan, A. C., "Silicon Nitride Products", French Patent 2,131,262 (December 15, 1972), assigned to Joseph Lucas (Industries), Ltd.**

Method of hot pressing shapes from mixtures of powdered Si_3N_4, MgO, and binder. Dimensional ratio of part remains unchanged during pressing. Suggests turbine blades be made this way.

682. **May, E.R.W., "Joining Silicon Structural Units", German Patent 1,943,802 (March 5, 1970), assigned to the National Research Development Corporation.**

Structural units are made from Si powder by pressing, sintering, or partly nitriding, followed by coating with a low-viscosity mixture of 1.0% aqueous NH_4 alginate and Si powder of <40 μm diameter, then pressed together under low pressure and dried at ~100 C. Sintering at 1350-1450 C in a N atmosphere gives a homogeneous Si_3N_4 ceramic substance. The transverse breaking strength at the joint at room temperature is ~42 kg/cm^2 (600 psi).

683. **Feller, F., "Ceramic Seals for a Rotary Piston Engine", German Patent 2,006,642 (July 26, 1973), assigned to Rolls-Royce, Ltd.**

A seal made from Si_3N_4 hot pressed with MgO.

684. **Phillips, J.G.R., and Brennan, A. C., "Silicon Nitride Products", German Patent 2,112,396 (October 7, 1971), assigned to Joseph Lucas (Industries), Ltd.**

Method of manufacturing Si_3N_4 products as sheets with a modulus of rupture of ~21-24 kg/mm^2, by mixing powdered Si (3 μm grain size) polymeric dispersion, as acrylic latex (Acronal 4D) in H_2O, shaping the product before or after removal of a dispersing agent, decomposing the polymer, and nitriding the residue.

685. **Washburn, M. E., "Silicon Nitride Oxide Refractory Molds", German Patent 2,132,347 (January 5, 1972), assigned to the Norton Company.**

Preparation of crack-free Si_2ON_2 molds by nitriding compacted mixtures of Si, SiO_2, and CaO.

686. **German Patent 2,134,072 (January 20, 1972). (See U. S. Patent 3,839,540, Entry No. 574)**

687. **Lumby, R. J., and Coe, R. F., "Silicon Nitride", German Patent 2,134,073 (January 20, 1972), assigned to Joseph Lucas (Industries), Ltd.**

Compacts of high strength were manufactured from powdered Si_3N_4 containing >10% β-phase by adding 10% clinoenstatite and (or) forsterite or MgO and SiO_2 in stoichiometric amounts for their formation. Composite compacts were made by pressing the powdered Si_3N_4-MgO-SiO_2 mixture onto a Si_3N_4 substrate or by pressing Si_3N_4 elements connected with a Si_3N_4-MgO-SiO_2 paste. Si_3N_4 of 75 μ average particle size containing 80% β-phase and 10% clinoenstatite were ground to 1 μm average particle size and compacted at 1750 C and 2.81 kg/mm^2 to give elements of theoretical density 3.2 g/cm^3 and modulus of rupture 56-84 kg/mm^2 at room temperature, which are comparable to those from α-phase powder.

688. **German Patent 2,135,648 (January 25, 1972). (See U. S. Patent 3,819,787, Entry No. 566)**

689. **German Patent 2,147,513 (March 30, 1972). (See U. S. Patent 3,839,541, Entry No. 575)**

690. **Fickel, A., and Petzenhauser, I., "Molded Products of Silicon Nitride and Silicon Nitride Oxide", German Patent 2,149,735 (April 12, 1973), assigned to Annawerk GmbH.**

Hot pressing of α-phase powders of Si_3N_4 or Si nitride oxide obtained from thermal decomposition of $SiCl_4$-NH_3 reaction products. 5% addition of MgO was used to produce dense Si_2ON_2.

691. **German Patent 2,152,066 (April 27, 1972). (See U. S. Patent 3,811,928, Entry No. 564)**

692. **German Patent 2,156,592 (May 25, 1972). (See British Patent 1,357,099, Entry No. 641)**

693. **Smith, D. W., and Lumby, R. J., "Hot-Pressing of Silicon Nitride Parts", German Patent 2,236,585 (February 8, 1973), assigned to Joseph Lucas (Industries), Ltd.**

Method of making shaped parts of Si_3N_4, for example conic sections, by hot pressing in shaped BN molds.

694. **Fickel, A., Gugel, E., and Leimer, G., "Improvement of Bending Strength of Hot Pressed Silicon Nitride and Silicon Nitride-Silicon Oxynitride Molded Products", German Patent 2,258,762 (June 12, 1974), assigned to Annawerk GmbH.**

Method of improving the bending strength of hot-pressed Si_3N_4 and Si_3N_4-Si_2ON_2 by annealing 2-40 hours at 1380-1700 C in vacuo or under N or Ar.

695. **German Patent 2,262,785 (July 5, 1973). (See U. S. Patent 3,903,230)**

696. **Jack, K. H., and Wilson, W. I., "Ceramics", German Patent 2,300,547 (July 19, 1973), assigned to Joseph Lucas (Industries), Ltd.**

Formation of Si, Al, O, N compounds by hot pressing Al_2O_3-Si_3N_4 mixtures in graphite dies with BN protective coatings. Specimen pressed at 3.9 kg mm^{-2} for 1 hour at 1700 C and then heated ½ hour at 2000 C was single phase.

697. **German Patent 2,301,426 (July 26, 1973). (See British Patent 1,405,171, Entry No. 677)**

698. **German Patent 2,302,202 (August 16, 1973). (See British Patent 1,359,896, Entry No. 643)**

699. **Richerson, D. W., and Washburn, M. E., "Dense Silicon Nitride Articles Containing Magnesium Silicate", German Patent 2,302,438 (July 26, 1973), assigned to the Norton Company.**

Hot pressing of Si_3N_4 with $MgCO_3$ additive.

700. **German Patent 2,316,348 (October 18, 1973). (See U. S. Patent 3,892,835, Entry No. 585)**

701. **Washburn, M. E., "Silicon Nitride Molded Products", German Patent 2,330,595 (January 3, 1974), assigned to the Norton Company.**

Formation of Si_3N_4 by reaction sintering Si powder compact in an atmosphere of N-NH_3. Si particle size was 2 μm, average, and 10 μm, maximum. Heating was done for 24 hours in 100 C steps from 1200-1450 C.

702. **Surrall, A. J., "Joining of Silicon Nitride Ceramic Parts", German Patent 2,338,230 (February 14, 1974), assigned to British Leyland Truck and Bus Division, Ltd.**

Si_3N_4 parts were soaked in an aqueous solution of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, dried and heat treated to yield Mo coatings. Parts were joined by putting additional coatings of Ag or Ni on surfaces and then heating in a reducing atmosphere.

703. **Applin, M., Krall, F., and Nesse, T., "Flat Moldings of Silicon Nitride by Pressing Powder or Granulates", German Patent 2,343,680 (April 24, 1975), assigned to Deutsche Gold-und Silber-Scheideanstalt vorm. Roessler.**

Hot pressing of Si_3N_4 plates in dies using embedded heaters.

704. **Church, P. K., and Knutson, O. J., "Sealing, Hardening, and Strengthening Moldings and Surfaces With Interconnected Porosity", German Patent 2,346,918 (April 4, 1974), assigned to Kaman Sciences Corporation.**

A porous Si_3N_4 part is impregnated with H_2CrO_4, heated to 677 C, and cooled. The cycle is repeated 13 times to produce a Cr oxide-containing body with Rockwell 15N hardness of 94-97.

705. **Dawohl, W., Doerre, E., Sturhahn, H., and Siefer, F., "Dense Moldings of Silicon Nitride", German Patent 2,349,277 (April 24, 1975), assigned to Feldmuehle Anlagen-und Produktionsgesellschaft mbH.**

Method of preparing dense Si_3N_4 shapes, especially turbine blades, by shaping powdered starting material with plasticizers and isostatically hot pressing at $\geqslant$1500 C.

706. **Lumby, R. J., and Horsley, R. F., "Silicon Nitride Powder", German Patent 2,350,031 (April 18, 1974), assigned to Joseph Lucas (Industries), Ltd.**

Method of preparing primarily α-Si_3N_4 powder by treating Si particles in a fluidized bed with a gas mixture (90% N-10% H) at temperatures $\leqslant$1300-1400 C. The supply of N is adjusted by the valves controlling the parts that admit the reacting mix.

707. **Fickel, A., "Hot-Pressed Dense Silicon Nitride", German Patent 2,351,161 (April 30, 1975), assigned to Annawerk GmbH.**

Molded bodies of hot-pressed dense Si_3N_4 and/or Si_2ON_2 containing SiC were prepared by firing a mixture Si powder and C in a N atmosphere at 1100-1450 C, pulverizing and hot pressing with an oxide pressing aid, as MgO.

708. **Fickel, A., "Reaction-Sintered Porous Silicon Nitrides", German Patent 2,351,162 (April 30, 1975), assigned to Annawerk GmbH.**

Reaction-sintered Si_3N_4 bending test specimen (porosity 28%) was infiltrated with Me polysilicate in vacuo at room temperature, dried, and annealed at 1050 C resulting in 5.5% weight gain, decrease in porosity, and ~9% increase in cold bending strength.

709. **Fickel, A., "Hot-Pressed Silicon Nitride", German Patent 2,351,163 (April 30, 1975), assigned to Annawerk GmbH.**

Si_3N_4 is hot pressed using glassy additives that are subsequently converted to glass ceramics by recrystallization anneal at 800 C.

710. **Masaki, H., "Sintered Silicon Nitride Ceramics", German Patent 2,353,093 (May 2, 1974), assigned to Toyota Central Research and Development Laboratories, Inc.**

Hot-pressing of Si_3N_4 powder and Al_2O_3, MgO, Cr_2O_3, Y_2O_3, ZnO, NiO, TiO_2, and SnO_2.

711. **Parr, N. L., "Silicon Nitride Ceramics", German Patent 2,356,921 (May 30, 1974), assigned to the National Research Development Corporation.**

Method of preparing Si_3N_4 ceramics of approximate theoretical density by compacting Si powder, reaction sintering in N for ~12 hours at 1200-1350 C, and compacting in a BN-coated graphite mold at 1600-1850 C and 2.35 kg/mm^2 after impregnating with 1-5 v/o MgO as flux, Additions of MgO, SiC, BN, graphite and Fe improved the high temperature, bearing, wear, and impact properties.

712. **Caws, R. B., and McQuillan, A. D., "Chromium Oxide Treatment of Porous Silicon Nitride", German Patent 2,360,434 (June 12, 1974), assigned to Advanced Materials Engineering Ltd.**

Cr oxide surface coatings on porous Si_3N_4 decrease porosity and increase hardness and oxidation resistance.

713. **Richerson, D. W., "Silicon Nitride Sintered Products", German Patent 2,412,339 (September 19, 1974), assigned to the Norton Company.**

Materials comprising Si_3N_4 or Al-Si oxynitride and SiC sintered with MgO sintering aid.

714. **Fickel, A., Gugel, E., and Kessel, H., "Silicon Nitride Moldings", German Patent 2,412,637 (October 16, 1975), assigned to Annawerk Keramische Betriebe GmbH.**

Parts comprising hot-pressed and reaction-sintered Si_3N_4.

715. **O'Neill, J. S., "Sintered Silicon Nitride Parts", German Patent 2,415,730 (October 10, 1974), assigned to British Leyland Ltd.**

Production of parts by injection molding.

716. **Mangels, J. A., "Silicon Nitride Articles", German Patent 2,451, 581 (May 7, 1975), assigned to Ford-Werke A.G.**

Method of producing Si_3N_4 articles by injection molding a mixture of Si powder and a thermoplastic material, heating to burn out the plastic and further heating in a N atmosphere to form the nitride.

717. **Ezis, A., Herrmann, E., and Nicholson, J. M., "Silicon Nitride Articles", German Patent 2,454,147 (May 15, 1975), assigned to Ford-Werke A.G.**

Slip casting of Si with control of particle size, solid content, and pH of slip. The latter contains Si, Fe_2O_3, and monoethanolamine in H_2O.

718. **Ezis, A., "Silicon Nitride Articles", German Patent 2,458,682 (July 3, 1975), assigned to Ford-Werke A. G.**

Injection-molded and sintered Si powder preform is coated with Si slip before nitriding.

719. **Fisher, E. A., Goodyear, M. U., McLean, A. F., and Styhr, K. H., "Silicon Nitride Molding", German Patent 2,458,688 (July 3, 1975), assigned to Ford-Werke A.G.**

Method of making parts of a gas-turbine rotor by mixing 60-6 v/o powdered Si (particle size 10-15 μ) with a thermoplastic resin, injection molding, burning out the resin at 350 C, and nitriding to produce Si_3N_4.

720. **Mutsuddy, B. C., Jefferson, P., and Errington, P. A., "Marking Silicon Nitride", German Patent 2,510,027 (September 11, 1975), assigned to Advanced Materials Engineering, Ltd.**

Method of marking Si_3N_4 by applying a mixture consisting of one or more metal oxides and/or a starting material capable of forming such oxides, a liquid vehicle (as H_2O) and a binder, and calcining the coated nitride.

721. **Olson, B. A., and Weaver, G. Q., "High-Strength Refractory Products Based on Silicon Nitride", German Patent 2,522,253 (December 4, 1975), assigned to the Norton Company.**

Hot pressing of Si_3N_4 with CeO_2 additive.

722. **Ishii, T., Nishida, K., Komatsu, M., and Tsuge, A., "Silicon Nitride Sintered Material", German Patent 2,528,869 (January 8, 1976), assigned to Tokyo Shibaura Electric Company, Ltd.**

Hot pressing of Si_3N_4 with Group IIIa metal oxide additives, specifically Y_2O_3.

723. **Henney, J. W., and Wilks, R. S., "Porous Silicon Nitride Articles", German Patent 2,540,015 (March 25, 1976), assigned to the United Kingdom Atomic Energy Authority.**

Method of reducing the gas permeability of porous Si_3N_4 moldings by partially or completely filling the open pores with components that form cordierite or a borosilicate glass in the pores.

724. **Tanba, S., Arakawa, K., and Sugiura, K., "Refractory Material Based on Silicon Nitride Containing Titanium Oxide", Japanese Patent 72 11,803 (April 13, 1972), assigned to Toshiba Ceramics Company, Ltd.**

Method of making a Si_3N_4 refractory by sintering Si_3N_4-TiO_2 powder mixtures in N or oxidizing atmospheres at 1400 C.

725. **Inoue, K., and Saito, S., "Preparation of Sintered Nitride Materials by a Spark Isostatic Press", Japanese Patent 72 14,125 (April 27, 1972), assigned to Inoue Japan Research, Inc.**

Method of preparing Si_3N_4 of various porosities by spark isostatic pressing of Si powder with stoichiometric amounts of N introduced into the press. Use of pure N produces a nitride with zero porosity and the porosity is controlled by adding He to N. When a mixture of O and N was used a nitride-oxide composite was formed.

726. **Niwa, S., Oki, K., Arakawa, Y., and Watanabe, T., "Refractories Containing Silicon Nitride", Japanese Patent 72 23,167 (June 28, 1972), assigned to Toshiba Ceramics Company, Ltd.**

Sintered Si_3N_4 refractories containing SiO_2 and various sintering aids such as $CaSiO_3$, Al_2O_3 cement, bentonite, and amorphous SiO_2.

727. **Yoneya, K., and Inoue, H., "Hard Refractory Composites Based on Nitride or Carbide of Aluminum, Silicon, or Boron", Japanese Patent 73 07,486 (March 6, 1973), assigned to Tokyo Shibaura Electric Company, Ltd.**

Fibrous composites made by mixing nitrides or carbides of Al, Si, or B with 15 m/o R_2O_3 (R = Y, Sc, Ta, or Ce) and sintering in N atmosphere at temperatures to 1700 C.

728. **Takase, S., and Ito, S., "Silicon Nitride", Japanese Patent 73 22,919 (July 10, 1973), assigned to Shinetsu Chemical Industry Company, Ltd.**

Diatomaceous earth (96% SiO_2) is mixed with C and nitrided to yield Si_3N_4, SiC, and Si_2ON_2.

729. **Tsuge, A., Komeya, K., Inoue, H., and Ota, H., "Heat-Resistant Inorganic Fiber-Reinforced Composite Materials", Japanese Patent 73 32,107 (April 27, 1973), assigned to Tokyo Shibaura Electric Company, Ltd.**

Powder containing at least one component selected from AlN, Al_4C_3, Si_3N_4, SiC, B_4C, and BN and at least one component selected from ThO_2, PaO_2, UO_2, BeO, SiO_2, and TiB_2 ~1-15 m/o was sintered in a nonoxidizing atmosphere to produce a fibrous structure.

730. **Tsuge, A., Inoue, H., Nishida, K., and Komatsu, M., "Heat-Resistant Reinforced Ceramics", Japanese Patent 73 32,110 (April 27, 1973), assigned to Tokyo Shibaura Electric Company, Ltd.**

Powder containing at least one component selected from AlN, Al_4C_3, SiC, Si_3N_4, B_4C, and BN (96-99% w/o) and at least one component selected from Y_2O_3, ThO_2, Sc_2O_3, La_2O_3, and Ce_2O_3 (0.1-4.0 w/o) was hot pressed in a nonoxidizing atmosphere.

731. **Unchara, H., and Oyama, Y., "Ceramic Sintered Body", Japanese Patent 73 76,914 (October 16, 1973), assigned to Tokyo Central Research and Development Laboratories, Inc.**

Powder mixture of 40-90 m/o AlN, 2-40 m/o SiO_2, and 0-30 m/o Si_3N_4 is hot pressed at 1650-2000 C to give dense material resistant to corrosion by molten glass at 1400 C.

732. **Kamigaito, O., and Oyama, Y., "Ceramic Sintered Body Containing Silicon Nitride, Gallium Oxide, and Aluminum Nitride", Japanese Patent 73 78,211 (October 20, 1973), assigned to Tokyo Central Research and Development Laboratories, Inc.**

Powder mixture of 15-90 m/o Si_3N_4, 10-60 m/o Ga_2O_3, and 0-68 m/o AlN is heated with or without pressure at 1650-2000 C to give dense body with expansion coefficient of 2.50×10^{-6} C.

733. **Kamigaito, O., and Oyama, Y., "Ceramic Sintered Body Containing Silicon Nitride, Germanium Oxide, and Aluminum Nitride", Japanese Patent 73 78,213 (October 20, 1973), assigned to Tokyo Central Research and Development Laboratories, Inc.**

Sintered ceramic formed by heating with or without pressure at 1650-2000 C powder mixture comprising 45-90 m/o Si_3N_4, 9-55 m/o GeO_2, and 0-20 m/o AlN.

734. **Komeya, K., Tsuge, A., and Inoue, H., "Heat Resistant Composite Materials from Silicon Nitride", Japanese Patent 73 79,216 (October 24, 1973), assigned to Tokyo Shibaura Electric Company, Inc.**

Method of preparing refractory composite materials with high strength by sintering Si_3N_4 $\geqslant$80 w/o and Al_2O_3 0.1-20 w/o at 1500-1800 C for 10-240 minutes in a nonoxidizing atmosphere. The composites are used for turbine parts and wear-resistant tools.

735. **Koyama, H., and Habata, H., "Silicon Nitride Whiskers", Japanese Patent 74 27,755 (July 20, 1974), assigned to Kanebo, Ltd.**

Method of preparing Si_3N_4 whiskers is described in which Si is reacted with gas mixture containing N_2 and/or NH_3 together with Cl and/or HCl at 860 C. The conversion rate was 78.2% and the whiskers were 0.01-1.0 μm diameter and 1.0-18 mm long with a tensile strength of 1400 kg/mm^2.

736. **Motoi, S., and Hidaka, S., "Silicon Nitride", Japanese Patent 74 45,000 (April 27, 1974), assigned to Onoda Cement Company, Ltd.**

Amorphous SiO_2 with absorbed F (acid fluoride or fluorosilicate) was mixed with carbonaceous matter and heated at 1300-1500 C in a N atmosphere to produce Si_3N_4.

737. **Kuratomi, T., "Silicon Nitride and Chromium Sintered Product", Japanese Patent 74 47,913 (April 24, 1976).**

Method of preparing a Cr-dispersed Si_3N_4 sintered material from CrN, Si, and Si_3N_4 by controlled heat treatment.

738. **Kamigaito, O., Masaki, H., and Kandori, T., "Abrasion- and Oxidation-Resistant Ceramic Sinter", Japanese Patent 74 76,911 (July 24, 1974), assigned to Toyota Central Research and Development Laboratories, Inc.**

Hot-pressed body comprising 25-40 m/o AlN, 10-30 m/o SiO_2, and balance Si_3N_4 had low porosity and good abrasion resistance.

739. **Kuratomi, T., "Molding of Silicon Nitride Powder", Japanese Patent 74 81,749 (January 28, 1976).**

Method of compacting powdered Si_3N_4-TiO_2-Ti and paraffin at 2000 kg/cm^2 and heating to 1700 C in H to produce a Si_3N_4 cermet with high strength and toughness. Other metal-oxide combinations may also be used.

740. **Kamigaito, O., Masaki, H., and Kandori, T., "Silicon Nitride-Based Ceramics", Japanese Patent 74 88,917 (August 26, 1974), assigned to Tokyo Central Research and Development Laboratories, Inc.**

Oxidant-resistant, high strength ceramic products consisting of Si_3N_4 and TiN were produced by mixing powder Si_3N_4, AlN, and TiO_2, molding, and sintering in an nonoxidizing atmosphere at 1650-1800 C or by hot pressing at 1700 C.

741. **Motoyoshi, K., "Aluminum-Silicon-Aluminum Nitride-Silicon Nitride-System Composite", Japanese Patent 74 107,307 (October 11, 1974), assigned to Sumitomo Electric Industries, Ltd.**

Al-Si-AlN-Si_3N_4-system composites were made by adding 0-10% Cu or Mg, presintering, heating in N at 900 C, and hot forging.

742. **Motoyoshi, K., and Hase, S., "Aluminum-Silicon Nitride Composite", Japanese Patent 74 108,116 (October 15, 1974), assigned to Sumitomo Electric Industries, Ltd.**

Al-Si-Si_3N_4 mixture was presintered in N at 600 C, hot forged, and heated in H at 600 C for 1 hour to obtain a composite.

743. **Komeya, K., Tsuge, A., and Nishida, K., "Silicon Nitride-Based Refractory Composite", Japanese Patent 74 110,708 (October 22, 1974), assigned to Tokyo Shibaura Electric Company, Ltd.**

A mixture containing 80 w/o powder α-Si_3N_4, 10 w/o Y_2O_3, 10 w/o Al_2O_3 with 5% stearic acid as a binder was molded and sintered in a N atmosphere at 1700 C for 2 hours to obtain a refractory composite.

744. **Ohgo, K., Naito, K., and Masaki, H., "Silicon Nitride Based Cutting Tool Materials", Japanese Patent 74 113,803 (October 30, 1974), assigned to Toyota Central Research and Development Laboratories, Inc.**

Sintered products containing 60-90 m/o Si_3N_4 and the balance MgO, ZnO, and/or NiO and Al_2O_3, and Cr_2O_3, Y_2O_3, and/or TiO_2 in spinal state and having diameter $\geqslant$3.10 g/cm^3 high abrasion resistance, and useful for cutting tool materials for hypereutectic Al-Si alloys.

745. **Kaneko, Y., Komiyama, Y., Kondo, K., Murakami, H., Noda, F., and Tsuzuki, Y., "Metal-Impregnated Porous Material", Japanese Patent 74 123,910 (November 27, 1974), assigned to Toyota Motor Company, Ltd.**

Pressure infiltration of Al into porous Si_3N_4 compact.

746. **Nishida, K., and Nakamura, K., "Silicon Nitride Sintered Product", Japanese Patent 74 128,915 (December 10, 1974), assigned to Tokyo Shibaura Electric Company.**

Si_3N_4 hot pressed/sintered material containing SiO_2, Al_2O_3, TiO_2, and optionally oxides of Li, Be, Mg, Ca, Sr, Cd, Ba, Mn, Fe, Co, and Ni.

747. **Komiyama, Y., Kondo, K., Noda, F., Uchida, K., and Tsuzuki, Y., "Impregnation of Sintered Metals, Ceramics, and Cermets With Metals", Japanese Patent 74 128,917 (December 10, 1974), assigned to Toyota Motor Company, Ltd.**

Use of fluxes, e.g., aqueous solution of NaCl and NaF, to improve wetting and infiltration of porous Si_3N_4 with metals, e.g., Al alloy. Bend strength of material impregnated with latter alloy was 400 M Pa.

748. **Uchiyama, H., and Tate, T., "Fibers of Silicon Nitride", Japanese Patent 75 04,480 (February 19, 1975), assigned to Mitsui Mining and Smelting Company, Ltd.**

Si_3N_4 fibers prepared by heating Si or Si compound with catalyst and reducing compound at 1300-1500 C in N. Catalyst may be elements or compounds of Ti, Zr, etc., and reducing compound C, graphite, or coke.

749. **Azuma, N., Yamada, R., Arai, Z., and Hayashi, H., "Fibrous Silicon Nitride by Reaction of Silicon-Carbon-Melamine Compacts With Nitrogen-Nitric Oxide-Hydrogen Mixture", Japanese Patent 75 21,160 (July 21, 1975), assigned to the Agency of Industrial Sciences and Technology.**

Title reactants yield SiO which is reduced to Si which reacts with N to form predominately α-Si_3N_4 whiskers at 1200-1350 C, and β-Si_3N_4 whiskers at ~1450 C.

750. **Niwa, S., and Arakawa, K., "Silicon Nitride Refractory Substance", Japanese Patent 75 27,852 (September 10, 1975), assigned to Toshiba Ceramics Company, Ltd.**

Method of preparing a Si_3N_4 refractory by mixing 95 w/o Si_3N_4 with 5 w/o clay, to be used in steel ingot manufacture and in a furnace for melting metals.

751. **Azuma, N., Yamada, T., and Hayashi, H., "Fibrous Silicon Oxynitride (Si_2ON_2)", Japanese Patent 75 29,498 (March 25, 1975), assigned to the Agency of Industrial Sciences and Technology.**

Fibers of Si_2ON_2, 5-15 μm diameter times 5-200 μm long were obtained by adding a heavy metal (as Fe, Mn, or Cu), or its salt, to a mixture of Si and SiO_2 and heating at $\leqslant$1420 C in N or a H containing N gas stream.

752. **Imai, T., "Silicon Nitride-Based Super-Hard Composite for Watch Case", Japanese Patent 75 55,607 (May 15, 1975), assigned to Suwa Seikoska Company, Ltd.**

Si_3N_4 is mixed with 0.1-10% Group IIIB and IVB metal oxides followed by hot pressing to obtain super hard composites, with Vickers hardness 1500-1600.

753. **Kamigaito, O., Oyama, Y., and Masaki, H., "Silicon Nitride Refractories", Japanese Patent 75 82,109 (July 3, 1975), assigned to Toyota Central Research and Development Laboratories, Inc.**

A mixture of Si, Al, Al_2O_3, and Fe_2O_3 was fired under N at 1350 C. Resulting powder was formed into crucible and sintered at 1600 C to give a product with 7% porosity. Al was unsuccessfully melted in crucible. Patent also includes other refractory compositions.

754. **Kamigaito, O., Masaki, H., and Kandori, T., "Manufacture of Silicon Nitride Sintered Body", Japanese Patent 75 128,708 (October 11, 1975), assigned to Toyota Central Research and Development Laboratories, Inc.**

Hot-pressed material comprising Si_3N_4, SiO_2, and Y_2O_3. AlN may also be added.

755. **Kamigaito, O., Masaki, H., and Kandori, T., "Abrasion-Resistant Sintered Ceramic Product", Japanese Patent 75 134,011 (October 23, 1975), assigned to Toyota Central Research and Development Laboratories, Inc.**

Si_3N_4, AlN, SiO_2 mixture that may be sintered or hot pressed. Data are given for hot-pressed material.

756. Futamura, O., Kato, T., and Nozaki, S., "Silicon Nitride Porcelain Products", Japanese Patent 75 149,710 (December 1, 1975), assigned to NGK Spark Plug Company, Ltd.

Si_3N_4 (60-95 parts) was mixed with Al_2O_3-SiO_2-alkaline earth metal oxide mixture (5-40 parts), shaped and sintered at 1580 C to obtain a Si_3N_4-based porcelain product having high strength, small thermal expansion coefficient, and good electrical insulating properties.

757. Inomata, Y., "Silicon Nitride Sintered Body With Silicon Coating", Japanese Patent 75 153,019 (December 9, 1975), assigned to the National Research Institute for Metals.

A 100 μm Si layer was formed on porous Si_3N_4 by heating in contact with Si powder in N for 15 minutes at 1450 C.

758. Nishida, K., Tsuge, A., Ishii, T., and Komatsu, M., "Strengthening Silicon Nitride Materials", Japanese Patent 76 02,712 (January 10, 1976), assigned to Tokyo Shibaura Electric Company, Ltd.

High-strength sintered Si_3N_4 products by mixing raw Si_3N_4 with Group IIA and VI metal oxides and hot pressing in the presence of AlN, e.g., compact is coated with 5 mm AlN and pressed at 1750 C.

759. Kuratomi, T., "High-Strength Shaped Silicon Nitride Product", Japanese Patent 76 28,105 (March 9, 1976).

Reaction-sintered Si_3N_4 containing various oxides such as TiO_2, etc.

760. Komeya, K., and Inoue, H., "α-Silicon Nitride", Japanese Patent 76 28,598 (March 10, 1976), assigned to Tokyo Shibaura Electric Company, Ltd.

Method of preparing α-Si_3N_4 from a mixture of pure SiO_2 and C in a mole ratio 1:5, at 1300-1400 C in an atmosphere of N or NH_3 and then oxidizing the excess C at 550-700 C.

761. Motoi, S., "Silicon Nitride", Japanese Patent 76 28,599 (March 10, 1976), assigned to Onada Cement Company, Ltd.

Method of preparing dense Si_3N_4 by mixing SiO_2 with Fe_2O_3 and C and heating in a N atmosphere.

762. Kuratomi, T., "Silicon Nitride Compacts of Sintering", Japanese Patent 76 41,011 (April 6, 1976).

Method of forming a Cr-dispersed Si_3N_4 by sintering Si, Cr, and Si_3N_4 at 1500 C in N and heating at 1800 C in N to yield dispersed Cr phase.

763. Kamigaito, O., "Silicon Nitride Powder", Japanese Patent 76 48,799 (April 27, 1976), assigned to Tokyo Research and Development Laboratories, Inc.

Powdered Si containing O as SiO_2 or Si_2ON_2 and C or SiC was heated to 1200-1420 C in a N atmosphere to convert metallic Si to α-Si_3N_4.

764. **Kamigaito, O., and Doi, H., "α-Silicon Nitride", Japanese Patent 76 48,800 (April 27, 1976), assigned to Tokyo Research and Development Laboratories, Inc.**

Powdered Si and MgO were mixed and heated at 1250-1450 C in a N-H atmosphere to obtain α-Si_3N_4.

765. **Oki, K., Koide, K., and Sugiura, K., "Silicon Nitride Sintered Products", Japanese Patent 76 76,312 (July 1, 1976), assigned to Toshiba Ceramics Company, Ltd.**

Si or ferrosilicon powder is mixed with additives including Al_2O_3, Y_2O_3, Ce_2O_3, and La_2O_3, compacted, and nitrided.

766. **Samsonov, G. V., and Kazakov, V. K., "Shaped Articles", Russian Patent 321,514 (November 19, 1971).**

The method of producing shaped articles by pressing a mixture based on Si_3N_4 and oxides as Al_2O_3 and MgO with subsequent nitriding. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 48 (35), 87-88 (1971)]

767. **Kulikov, F. S., and Kuznetsov, V. K., "Silicon Nitride", Russian Patent 329,204 (February 9, 1972).**

Method of preparing Si_3N_4 during reprocessing of Fe containing >3% Si by blowing N through the vat is changed to produce Si_3N_4 as one of the reduction products by blowing N through at the beginning of melting and collecting Si_3N_4 formed in dust collectors or electrostatic precipitators. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 49 (7), 106 (1972)]

768. **Karpinos, D. M., Mikhashchuk, E. P., Grosheva, V. M., Agulov, I. I., Fenenko, A. I., Efimov, G. V., and Pilipovskii, Yu. L., "Refractory Material", Russian Patent 331,047 (March 7, 1972).**

A method of preparing a refractory material containing 50-90% Si_3N_4 and 10-50% dispersed α-Al_2O_3 with increased thermal stability and mechanical resistance. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 49 (9), 66 (1972)]

769. **Samsonov, G. V., and Kazakov, V. K., "Electroinsulating Thermostable Refractory Material", Russian Patent 346,289 (July 28, 1972).**

Method of producing a material containing Si_3N_4 30-89, SiC 1-60, and Al_2O_3 or MgO 10-15 m/o % having increased chemical and erosion resistance and mechanical strength. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 49 (23), 97 (1972)]

770. **Karpinos, D. M., Mikhashchuk, E. P., Grosheva, V. M., Pavlikov, V. N., Pilipovskii, Yu. L., Shamatov, Yu. M., and Klimenko, V. S., "Ceramic Material", Russian Patent 351,811 (September 21, 1972).**

Method of producing a ceramic material containing Si_3N_4 80-85 w/o and Cr_2O_3 15-20 w/o having increased mechanical strength and thermal stability. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 49 (28), 67 (1972)]

771. **Karpinos, D. M., Mikhashchuk, E. P., Grosheva, V. M., Pavlikov, V. N., and Volkogon, L. M., "Refractory Material", Russian Patent 353,930 (October 9, 1972).**

Method of producing a refractory material with increased thermal stability and impact strength containing Si_3N_4 80-85 and β-Al_2O_3 crystals 15-20 w/o. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 49 (30), 54 (1972)]

772. **Samsonov, G. V., and Kazakov, V. K., "Refractory Material", Russian Patent 374,256 (March 20, 1973).**

Method of preparing a refractory material containing Si_3N_4 30-99, BN 0.5-50, and SiC fibers 0.5-20 m/o. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 50 (15), 42 (1973)]

773. **Samsonov, G. V., and Kazakov, V. K., "Electroinsulating Refractory Material", Russian Patent 374,257 (March 20, 1973).**

Method of preparing an electroinsulating refractory material containing Si_3N_4 30-70 and TiO_2 30-70 w/o. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 50 (15), 42 (1973)]

774. **Samsonov, G. V., and Kazakov, V. K., "Refractory Material", Russian Patent 374,258 (March 20, 1973).**

Method of preparing a refractory material with increased mechanical strength, thermal stability, and erosion resistance containing Si_3N_4 40-98, SiC 1-45, and SiC fibers 1-15 w/o. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 50(15), 42 (1973)]

775. **Karpinos, D. M., Grosheva, V. M., Pilipovskii, Yu. L., Kondrat'ev, Yu. V., Shamatov, Yu. M., and Golenevich, V. A., "Refractory Material", Russian Patent 380,615 (May 15, 1973).**

A material of superior impact strength was produced from Si_3N_4 powder containing 15-20 w/o Si_3N_4 whiskers. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 50 (21), 81 (1973)]

776. **Samsonov, G. V., Kazakov, V. K., Grosheva, V. M., and Dubovik, T. V., "Refractory Material With Increased Density, Mechanical Strength, and Erosion Resistance", Russian Patent 386,874 (June 21, 1973).**

Method of producing a refractory material containing Si_3N_4 62-89.5 w/o, mullite crystal whiskers 2-29.5 w/o, and AlN 8-35.5 w/o. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 50 (27), 57 (1973)]

777. **Samsonov, G. V., and Kazakov. V. K., "Refractory Material", Russian Patent 389,058 (July 5, 1973).**

Addition of 20-79 m/o Al_2O_3 to material comprising 10-69 m/o BN and 10-69 m/o Si_3N_4. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 50 (29), 85 (1973)]

778. **Samsonov, G. V., Kazakov, V. K., Grosheva, V. M., and Gorodetskii, S. S., "Refractory Material", Russian Patent 389,061 (July 5, 1973).**

Method of increasing the density, mechanical strength, chemical resistance, and erosion resistance of a refractory material containing Si_3N_4 62-89.5 w/o and BN 8-35.5 w/o by adding mullite crystal whiskers 2-29.5 w/o. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 50 (29), 86 (1973)]

779. **Karpinos, D. M., Grosheva, V. M., Doroshenko, R. P., Pilipovskii, Yu. L., and Dobrovol'skii, A. G., "Refractory Material", Russian Patent 390,049 (July 11, 1973).**

Method of producing an impact resistant refractory material containing Si_3N_4 80-85 w/o and Al_2O_3 whiskers 15-20 w/o. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 50 (30), 70 (1973)]

780. **Samsonov, G. V., Kazakov, V. K., Kislyi, P. S., and Gorodetskii, S. S., "Refractory Material", Russian Patent 408,936 (November 30, 1973).**

Al_2O_3 (9.5-49 w/o) was added to composition containing Si_3N_4 (50-89.5 w/o) and TiO_2 (0.5-1.0 w/o) to increase density, mechanical strength, erosion, and chemical resistance. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 50 (48), 66 (1973)]

781. **Samsonov, G. V., Kislyi, P. S., and Gorodetskii, S. S., "Refractory Material", Russian Patent 422,705 (April 5, 1974).**

Method of increasing the mechanical strength, erosion, and heat resistance of Si_3N_4 refractory by adding mullite crystal whiskers (4.5-9.5 w/o) as well as MgO (4.5-15.0 w/o). [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 51 (13), 87-88 (1974)]

782. **Samsonov, G. V., Kazakov, V. K., and Kislyi, P. S., "Refractory Compositon", Russian Patent 427,913 (May 15, 1974).**

Refractory composition containing 63-96 w/o Si_3N_4, 3.5-33 w/o Al_2O_3, and 0.5-4.0 w/o SiO_2 for manufacturing of electrical insulating blanks. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 51 (18), 54 (1974)]

783. **Samsonov, G. V., Kazakov, V. K., and Kislyi, P. S., "Refractory Containing Graphite and a Silicon Nitride Coating", Russian Patent 445,635 (October 5, 1974).**

Refractory containing an intermediate layer of SiC to increase the adhesion of Si_3N_4 to graphite and its stability in corrosive media. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 51 (37), 59 (1974)]

784. **Samsonov, G. V., Kazakov, V. K., and Kislyi, P. S., "Refractory Material", Russian Patent 449,022 (November 5, 1974).**

Mullite crystal whiskers (4.5-9.5%) and Al_2O_3 (4.5-15%) were added to Si_3N_4 to produce a refractory having increased strength, erosion resistance, and heat resistance. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 51 (41), 42 (1974)]

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Includes ambient and high temperature data on fracture energy of Si_3N_4. Fracture energy was dependent upon microstructure, but it did not correlate with fracture strength.

788. Heung, L. K., "Ceramic Materials for Sliding Applications", unpublished Ph. D. dissertation, University of Rhode Island (1974).

Oxidation of hot-pressed Si_3N_4 was studied at 600-1450 C. Oxidation products include SiO_2 and Mg and Ca silicates. Wear Behavior and effects of oxidation on wear are also described. A novel surface parameter relating friction and wear characteristics is proposed and experimental methods are described.

789. Horsley, R. F., "The Formation of Silicon Nitride Ceramic By Reaction-Sintering", unpublished Ph. D. dissertation, University of Leeds (1971).

Kinetics of the reaction between Si and N were studied. Gas access shown to control nitridation in some cases. Effects of time, temperature, gas composition, surface area of powder, and solid phase impurites are also discussed. Reaction rate under certain conditions may be controlled by diffusion of N through a protective layer of β-Si_3N_4.

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Different morphologies of α- and β-Si_3N_4 examined by scanning electron, transmission electron, and optical microscopes were correlated with the processing conditions. Mechanisms are proposed for formation of most of the observed microconstituents. Models explaining the bonding in both the α- and β-phases are proposed.

791. Kiehle, A. J., "An Investigation of the High Temperature Chemical and Structural Stability of Hot Pressed Silicon Nitride", unpublished M. S. thesis, University of Rhode Island (1973).

Products of high temperature oxidation (to 1450 C) of hot-pressed Si_3N_4 were studied by X-ray diffraction and scanning electron microscopy. Products observed included amorphous SiO_2, cristobalite, and Mg silicates.

AUTHOR INDEX

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